VOL. XL. DECEMBER, 1908. NO. 6.

AMERICAN CHEMICAL JOURNAL

THE FRACTIONATION OF CRUDE PETROLEUM BY CAPILLARY DIFFUSION.

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When, in process of refinement, black vaseline is filtered through warm dry fuller's earth the first product is an oil perfectly liquid at ordinary temperatures, while the succeeding portions are progressively more viscous until quite hard vaseline is obtained. This observation, that a fractional separation of oils in vaseline had been effected, suggested to D. T. Day that a like result might be obtained with crude petroleum. He applied this method to a sample of the green crude petroleum from the "third sand" of Venango County, Pennsylvania, and found that light products, chiefly gasoline, first appeared when such crude oil was allowed to filter down through a long glass tube filled with granulated or powdered fuller's earth.[1]

Following this, a more elaborate system of specially constructed funnels, similar to those used by the refiners of vaseline in testing the comparative value of various fuller's earths, was used. The results of this work were briefly summarized in a paper upon the ability of petroleum to migrate in the

[1] P. Am. Phil. Soc., **36**, No. 154, 1897.

earth.[1] Engler later verified these results and showed that the separation was mechanical and that no oxidation was effected in the process. Day next used a large closed funnel of galvanized iron holding about one hundred pounds of fuller's earth. When crude petroleum was dropped slowly and regularly into this, quite light oils at first, followed by the usual succession of heavier oils, were obtained. As it was evident from this work that much of the oil passed through crevices without any change he tried the effect of reversing the route of the oil and of allowing it to diffuse upward through a tube packed tightly with fuller's earth. In such a tube the lighter constituents rose much more rapidly than the more viscous oils so that by separating the fuller's earth from different sections of the tube and displacing the oil by water, quite different oils were obtained from the upper and lower parts of the tube.

By using several tubes and uniting oils of the same specific gravity, oils of different grades can be collected in sufficient quantity to be fractionated again, and the process continued until oils result which are not altered by further passage through tubes filled with fuller's earth. At the suggestion and with the coöperation of Day, we have taken up this problem, with the results stated below.

The tubes used first were three feet long and one and one-eighth inches in diameter. They were closed at the lower end with corks, along the sides of which grooves had been cut, the top of the cork being covered with a bit of cotton cloth to prevent the earth from sifting out of the grooves. Such tubes filled with fuller's earth[2] were placed with their lower ends in an open dish of petroleum and the oil was allowed to rise.

At room temperatures (18°–22° C.) and atmospheric pressure, the rate of rise of crude petroleum in a tube filled with fuller's earth was very slow. In seven days the oil ascended but 73 cm. in one tube, while ten days in one case and seven in another were required for it to rise 59 cm. To study the

[1] Trans. Petroleum Congress, Paris (1900).

[2] The fuller's earth used in this work was kindly furnished by the Atlantic Refining Co., of Philadelphia.

effect of heat, a glass tube about three feet long and $1\frac{1}{8}$ inches in diameter was filled with earth and placed in a bottle holding about two liters of oil, and the whole heated by an electric stove by means of which temperatures considerably above those of the room could be maintained day and night. The temperature of the tube was kept between 40° and 70° for three days, in which time the oil rose 54.7 cm. in the tube; in another tube packed in all ways like the former but kept at room temperature (about 20°), the oil rose 46 cm. in the same length of time. With two tubes in which the earth was packed much less compactly, the time required for the oil to rise 54 cm. was four days for the tube at room temperature and two days for the one at 50° to 80°.

The rate of rise evidently was but little affected by heat, at least within this range of temperature, and higher temperatures could not be used without loss of the more volatile constituents of the oil.

The next attempt at increasing the rate of rise of the oil consisted in applying diminished pressure to the top of the tube, which reduced the time required for the oil to reach the top of a tube five feet long from several weeks to seventeen hours. If diminished pressure is continued after the oil has reached the top, provided the oil is not exhausted in the reservoir at the bottom, oil will be drawn over from the top of the tube. The specific gravity of the oil thus collected steadily rises as it comes over. The samples so obtained, however, stand under very low pressures for some time, which may cause a loss of their more volatile constituents. This suggested applying increased pressure to the oil in the reservoir rather than diminished pressure to the top of the tube, and an iron bomb, like those used for the transportation of mercury, was fitted with an iron pipe seven feet long to contain earth and a side arm at the bottom of the bomb to which a water column could be attached.

The bomb, which held about two liters, could be partly filled with petroleum and the pipe containing the earth screwed into the top. The side arm which opened into the bottom of the bomb could then be connected with the water pressure

so that the lower part of the bomb was filled with water which drove the petroleum upwards. The oil obtained at the top, however, was fractionated no further nor in any larger amounts than when the oil was not allowed to emerge from the top of the tube. The difficulty of setting up such a pressure apparatus with tight connections, as well as the range of pressure required—a column of water seven feet high being too great when the oil was just starting up the tube while a column thirty feet high was insufficient when it was near the top—made the use of this method impracticable.

To use diminished pressure, the earth in the tubes must not be packed so hard that the air just above the oil cannot be drawn through the earth above, nor must the earth be packed so loosely that the oil will rise as in a vacuum. The right degree of hardness is obtained by filling about a foot of the tube at a time and packing that much earth as hard as possible with a wooden rod tipped with a rubber stopper. If the tube, when pounded upon the floor, rings in the hand, the earth is apt to be packed too closely. Packing tubes may be much facilitated by filling several at once with a separate ramrod for each. By allowing a few minutes to elapse between successive liftings of the ramrod, in order that the air may escape and the fuller's earth settle, much labor is avoided.

The fuller's earth was first heated in shallow iron pans until it ceased to form geysers when stirred. The earth must be thoroughly cold before it is packed into tubes or the contraction is sufficient to allow the oil to run up the tube immediately when the air is exhausted.

The lower end of the tube is best closed with a cork with six or seven grooves cut along the side, and the inner end covered with a bit of cloth to keep the earth from sifting out of the grooves. At the top of the tube a bit of cotton waste below a rubber stopper will prevent any earth from being drawn up when the air is exhausted.

The tubes used first were three feet long and one and one-eighth inches in diameter and of glass. Much trouble was experienced on account of their breaking, not when in ser-

vice, but soon after they had been used. This was thought to be due to the age of the tubing, but the same happened with new tubes five feet long and one and one-fourth inches in diameter. Thinking that the iron scraper used to remove the earth from the tubes might be the cause, we tried a scraper made entirely of wood, but this did not decrease the breakage, it being nothing unusual on going to the laboratory in the morning to find that half of the tubes which had been emptied the day before were cracked.

It had been considered necessary to use tubes of glass in order that the height to which the oil had risen might be seen and that in removing the oil from the middle of the tube it might be scraped out to a sharp dividing line, since the level to which the oil has risen is the point from which all measurements should be made of sections into which the tube is to be divided. Tin tubes were used later to avoid the trouble experienced with glass tubes. These tin tubes were emptied by shaking the earth from the bottom into four thirty-centimeter cylinders of the same diameter as the tube, these cylinders being made of two curved pieces of tin held together by a cap at one end and a ring at the other. The cylinders containing the contents of the tube could be opened lengthwise and the earth divided into any desired lengths. Two glass tubes five feet long and one and one-fourth inches in diameter were set up in the same dish of petroleum with ten or twenty tin tubes of the same diameter, and five and one-half feet long, and when the oil stood at the top of the glass tubes the tin ones were opened. Glass tubes, of course, can be emptied as well as tin ones by shaking the contents from the bottom, and no more tubes broke after this method was adopted.

The level to which the oil will rise can be regulated by the amount of oil in which the tube is placed, and in the later work the adoption of this method did away with the use of glass tubes entirely. With nine hundred and fifty cc. the oil will rise to within 20 to 35 cm. of the top of a tube one and one-fourth inches in diameter and five and one-half feet long.

When the oily earth has been removed from the tube, the

oil may be separated by adding water. In the first experiments enough water was added to form a very thin mud which was thoroughly stirred by a small propeller driven by a water motor. The mixed earth, oil, and water were then poured into a large separating funnel and allowed to stand several minutes until the oil had collected at the top. The earth and water could then be drawn off and the pure oil left.

It was found later, however, that if less water is added to the earth as removed from the tubes, after standing a few minutes all the water will pass into the earth and this will be accompanied by the liberation of oil. Oil so liberated can then be poured off directly from the earth without the labor of churning. When water first begins to liberate oil, the earth is granular, whereas when more water has been added and the last of the oil recovered the earth has the consistency of a thin paste which will flow when the dish is inclined.

All the oil from the same section of a tube is of the same color irrespective of whether it is the first oil to separate when water is added or whether it does not separate until the last. It was assumed at first that all such oil which was obtained from the same section of earth had the same specific gravity whether it was the first or last replaced when water was added, but this was found later not to be the case.

The first oil to be collected, if taken in sufficiently small volume, is slightly heavier than the next portion. If too much is included in the first sample this will not be the case. Beginning with the second sample the successive portions of oil steadily increase in specific gravity, this gradual addition of water affording another means of fractionation in addition to the separating power of the earth. Both of these methods of separation have been combined in this investigation. The earth must be thoroughly mixed after each addition of water so that the layer of wet earth shall not isolate the oily earth from the water added.

The petroleum used was a dark green oil from Venango County, Pennsylvania, of specific gravity 0.810. When

950 cc. of this were drawn upwards in a tin tube five and one-half feet long the separation shown in Table I. was obtained.

Table I.—Single Tubes in the Crude Petroleum.

	(1)		(2)		(3)	
Time required	23.5 hrs.		17.5 hrs.		17.5 hrs.	
Distance from top of tube to oil when opened ...	31 cm.		28 cm.		28 cm.	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A, 8 cm. at top...	0.796	42	0.8012	30	0.8022	18
B, next 8 cm.....	0.808	45	0.804	37	0.803	35
C, next 18 cm....	0.8125	75	0.807	47	0.8075	66
	0.8137	24	0.809	22	0.810	25
D, next 30 cm....	0.815	130	0.8125	148	0.812	140
E, next 35 cm....	0.818	170	0.8185	190	0.8175	145
F, rest.....	0.8205	125	0.823	100	0.821	105
		611		574		534

The oil from section C was collected in two portions, the second being obtained by the addition of more water after the first lot of oil was poured off. Although 950 cc. of crude petroleum were used in each case, it will be noticed that the amount of oil recovered was much less than that. When several tubes were worked up together, in one case 9070 cc. of crude petroleum yielded 5951 cc. of oil, and in another case 8915 cc. gave 5415 cc.

To collect a sufficient quantity of oil several tubes were placed in the same vessel containing the petroleum, two of the tubes being of glass and the rest of tin. When the oil had reached the top of the glass tubes they and the tin ones were opened, and the earth from the same level in all the tubes was, mixed in tin pails. The oil was then liberated in several successive fractions by the addition of successive amounts of water. If the earth had been thoroughly mixed after each addition of water the various oils from the same lot of earth would increase regularly in specific gravity, instead of showing the variations which in many cases they do; *e. g.*, the first oil to be displaced by water in D and E of (4), in Table II., with so large volume, would not have been heavier than the suc-

ceeding oils if the water and earth had been thoroughly mixed before the oil was poured off. If we were to repeat the work, instead of using one common reservoir for all the tubes, we would use a separate reservoir for each tube, and open the tube when the oil in the reservoir was exhausted. This would do away with the use of glass tubes entirely, besides insuring that the level of the oil in each tube when opened would be practically the same. If a common reservoir is to be used the tubes should all be packed with practically the same degree of hardness if the oil is to ascend in all with equal rapidity, since the ascent in all tubes is checked at the same time, *i. e.*, when the oil in the reservoir is exhausted.

Diminished pressure was obtained by use of a Chapman water pump which reduced the pressure to from five to twelve cm. mercury when connected with a system of tubes. In the earlier work the pump was not run through the night. This is the reason why these lots of tubes required so much more time.

The earth from a tube was divided into six sections, the level to which the oil had ascended in the tube being taken as the point to be measured from. A, the top section, includes the eight cm. next the top; B, the next eight cm.; C, the next eighteen; D, the next thirty; E, the next thirty-five; while F includes what earth is left. F varies, of course, depending upon the height to which the oil has risen. In fractionating the crude petroleum in bulk, F was usually discarded since it was so viscous that it was deemed impossible to pass it through earth again. Records from several lots of tubes are given in Table II. The specific gravity was measured with a Westphal balance, the temperature being in every case exactly 20° C. While the fourth decimal place is not to be taken as strictly accurate, yet it is considered worth while to record it as giving a nearer approach to the truth than would result from the use of only three decimal places.

Table II.—First Fractionation of Crude Petroleum.

Tubes. Distance from level of oil to top of tube in cm.[1] Hrs. required.	(4) 2 glass, 8 tin. Glass, 0, 15. Tin, 40, 15, 24, 22, 28, 19, 24, 32. 54		(5) 2 glass, 7 tin. Glass, 0, 6.5. Tin, 26, 28, 18, 15, 28, 12, 24. 24		(6) 2 glass, 8 tin. Glass, 0, 12. Tin, 30, 28, 22, 30, 13, 12.[2] 54	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A	0.8015	50	0.804	100	0.805	65
	0.8005	350	0.8055	190	0.805	200
B	0.807	260	0.8085	220	0.807	140
	0.810	190	0.811	120	0.8097	125
C	0.809	100	0.8097	430	0.810	390
	0.809	400	0.8122	300	0.8135	380
	0.810	225				
	0.8115	260				
D	0.815	425	0.813	530	0.8133	610
	0.8145	625	0.8135	600	0.816	325
	0.8175	460	0.816	200	0.8175	435
					0.825	125
E	0.816	440	0.8162	480	0.816	850
	0.815	400	0.8162	725	0.8195	260
	0.821	830	0.819	390	0.821	330
					0.827	325

	(7) 2 glass, 7 tin. Glass, 0, 7. Tin, 25, 26, 23, 26, 28, 20, 28. 84		(8) 2 glass, 7 tin. Glass, 0, 5. Tin, 16, 34, 28, 15, 18, 23, 10. 48		(9) 2 glass, 7 tin. Glass, 8. 5, 15. Tin, 58. 31, 60, 40, 16, 53, 16. 117		(10) 2 glass, 9 tin. Glass, 0, 8. 5, Tin, 40, 32, 36, 26, 27, 27, 20, 25, 18. 84	
A	0.800	200	0.798	130	0.8025	175	0.7995	200
	0.802	115	0.801	130	0.8037	120	0.8037	160
							0.806	23
B	0.8042	200	0.803	155	0.8042	180	0.8085	125
	0.8048	200	0.8045	230	0.8078	215	0.810	275
							0.8112	23
C	0.808	330	0.8072	430	0.809	300	0.810	350
	0.8078	430	0.808	275	0.8095	440	0.812	525
	0.811	95	0.808	225	0.8127	100	0.8135	150

[1] The glass tubes are five feet long, the tin tubes five and one-half feet. Both are one and one-quarter inches in diameter.

[2] Record of distance lost for two tin tubes.

Table II. (Continued).

	(7) 2 glass, 7 tin. Glass, 0, 7. Tin, 25, 26, 23, 26, 28, 20, 28. 84		(8) 2 glass, 7 tin. Glass, 0, 5. Tin, 16, 34, 28, 15, 18, 23, 10. 48		(9) 2 glass, 7 tin. Glass, 8, 5, 15. Tin, 58, 31, 60, 40, 16, 53, 16. 117		(10) 2 glass, 9 tin. Glass, 0, 8, 5. Tin, 40, 32, 36, 26, 27, 27, 20, 25, 18. 84	
D	0.812	425	0.8117	420	0.812	390	0.8148	440
	0.812	625	0.812	580	0.8137	400	0.8175	700
	0.814	360	0.822	250[1]	0.8145	300	0.817	370
			0.8145	300	0.8155	200	0.817	200
			0.8177	42				
E	0.8172	240	0.8135	390	0.818	340	0.8197	315
	0.816	650	0.814	560	0.8197	240	0.8215	720
	0.8162	660	0.8248	390[1]	0.818	290	0.8223	570
	0.8195	300	0.817	230	0.818	350	0.821	215
			0.821	42				

	(11)[2] 2 glass, 8 tin. Glass, 0, 4. Tin, 0, 0, 0, 0, 20, 17, 7, 5. 39		(12)[3] 2 glass, 6 tin. Glass, 7, 13. Tin, 32, 19, 32, 35, 48, 29. 60		(13)[4] 2 glass, 9 tin. Glass, 2, 2.5. Tin, 17, 10, 11, 22, 16, 29, 8.5, 5, 5, 14. 20		(14) 2 glass, 9 tin. Glass, 0, 0. Tin, 20, 20.5, 13.5, 15, 14.5, 19, 8, 12, 14. 16.5	
A	0.799	80	0.798	150	0.8015	110	0.798	225
	0.802	180	0.801	140	0.8055	40	0.8005	110
					0.8028	125	0.8015	80
					0.8033	100		
B	0.807	200	0.8022	160	0.802	230	0.8015	210
	0.8115	140	0.806	105	0.8072	60	0.804	150
			0.8072	20	0.8085	50	0.8058	120
					0.8075	75		
C	0.810	300	0.807	400	0.806	340	0.8048	500
	0.811	490	0.809	200	0.808	220	0.8065	385
	0.8145	175	0.8115	60	0.8072	320	0.8075	225
					0.8097	150		

[1] These fractions stood uncovered on top of the earth overnight and consequently were exposed to considerable evaporation.

[2] During the night oil was drawn entirely through and out at the top of five tubes which were lost.

[3] Three other tubes were set up with these but when opened the oil in these was 81, 81, and 90 cm., respectively, from the top, so they were discarded. The unevenness between the tubes was probably caused by using in some of them earth which was not entirely cold.

[4] Beginning with lot (13) the pump was run continuously day and night.

Table II. (*Continued*).

	(11)[1] 2 glass, 8 tin. Glass, 0, 4. Tin, 0, 0, 0, 0, 20, 17, 7, 5. 39		(12)[1] 2 glass, 6 tin. Glass, 7, 13. Tin, 32, 19, 32, 35, 48, 29. 60		(13)[1] 2 glass, 9 tin. Glass, 2,12.5. Tin, 17, 10, 11, 22, 16, 29, 8.5, 5, 5, 14. 20		(14) 2 glass, 9 tin. Glass, 0, 0. Tin, 20, 20.5, 13.5, 15, 14.5, 19, 8, 12, 14 16.5	
D	0.8133	450	0.811	400	0.809	400	0.810	500
	0.8133	530	0.8097	420	0.8135	250	0.810	660
	0.816	290	0.811	290	0.8115	680	0.810	650
	0.8142	250	0.815	60	0.812	650	0.812	260
E	0.8172	400	0.815	260	0.813	400	0.8135	470
	0.818	520	0.8148	510	0.818	285	0.8155	530
	0.819	405	0.815	400	0.8167	700	0.8155	700
	0.8175	370	0.817	100	0.8167	805	0.8162	680

	(15) 2 glass, 9 tin. Glass, 0, 10. Tin, 32, 31, 23, 23, 24, 26, 9, 16, 14. 16.75		(16) 2 glass, 9 tin. Glass, 0, 5. Tin, 24, 19, 16, 15, 17, 23, 17, 4, 2. 16.5		(17) 1 glass, 9 tin. Glass, 14. Tin, 8, 27, 13, 6, 8, 0, 0, 0, 0. 17	
A	0.800	300	0.800	125	0.804	240
	0.805	95	0.8025	200	0.8055	120
			0.8028	80	0.8085	23
B	0.802	300	0.8042	245	0.812	220
	0.808	90	0.8065	100	0.812	155
	0.8055	120	0.810	110	0.8127	45
C	0.8065	800	0.8085	230	0.814	500
	0.810	350	0.8085	600	0.8125	450
			0.8115	210	0.815	40
D	0.8112	600	0.8117	435	0.814	540
	0.8142	525	0.8135	650	0.814	670
	0.8122	680	0.8137	370	0.8145	350
	0.8155	200	0.8148	350		
E	0.8145	740			0.817	740
	0.820	400	see		0.8172	750
	0.818	400	below			
	0.817	820				

[1] Foot-notes on preceding page.

Table II. (*Continued*).

	(18)[1]				(19)[1]			
	2 glass, 9 tin. Glass, 8, 5. Tin, 17, 2, 15. 19, 12, 22, 21, 0, 0. 21.5		2 glass, 9 tin. Glass, 14, 17. Tin, 30, 42, 39. 28, 35, 33, 42, 30, 42.		2 glass, 9 tin. Glass, 0, 0. Tin, 17, 11, 5. 18, 12, 15, 13, 18, 11. 23		2 glass, 8 tin. Glass, 0, 9. Tin, 13, 12. 23, 15, 19, 11, 13, 26.	
A	0.8005	425			0.806	200		
	0.8005	225			0.804	300		
	0.8015	190			0.8085	180		
B	0.803	320			0.8055	290		
	0.803	320			0.8072	175		
	0.8042	200			0.809	175		
	0.8055	75			0.807	200		
C	0.8078	475			0.809	570		
	0.8078	680			0.8097	930		
	0.808	500			0.8135	140		
	0.8085	200			0.813	100		
	0.8095	170						
	0.8105	150						
D	0.8117	420	0.8122	500	0.8128	560	0.8128	475
	0.8117	680	0.8125	500	0.813	725	0.813	740
	0.813	660	0.814	350	0.815	400	0.8185	180
	0.8155	90	0.817	40				
E	0.8158	1450			0.816	930		
	0.8158	1000			0.816	930		
	0.8165	420			0.8165	460		
	0.8175	350			0.8185	400		
	0.8187	500			0.8185	520		
					0.820	200		

To study further the fractionation on addition of water, E from lot 16 was collected in fourteen fractions. The weight of the earth impregnated with oil before any water had been added was 13.5 pounds, while the weight of the earth containing all the water added, but minus the oil, was 17.5 pounds. The earth was placed in a galvanized iron garbage pail and the water stirred in with an iron paddle. When the first portion of oil was liberated the mass was of the consistency of bran, but as more water was added it turned to a fluid paste. When water was added and the pail inclined, oil

[1] (18) and (19). Two reservoirs of crude oil were used but the earth from all 22 tubes was worked up together. Grade D from all 22 tubes was first united and then, for convenience in working, divided into two portions.

would continue to drain for half an hour or longer before the addition of more water became necessary. The oil which was liberated by one lot of water, therefore, could be collected in several portions, and this was done to see whether the oil which comes off immediately after the addition of water is the same as that which drains later. The fractions included within the brackets were liberated by one addition of water.

	Sp. gr.	cc.
I	0.821	25
II	0.818	70
	0.818	70
	0.8193	250
III	0.818	395
	0.818	350
	0.818	460
	0.820	60
IV	0.8208	575
	0.8222	55
V	0.824	170
	0.828	16
VI	0.827	95
	0.830	45

This phenomenon of a first fraction of higher specific gravity than the ones immediately following occurs regularly if the proper amount of water is added to liberate a first fraction of small enough volume. As the volume of the fraction first obtained becomes larger its specific gravity approaches nearer to that of the second fraction, and falls below it if its volume is made too large.

The range of specific gravity covered by this first fractionation of the crude petroleum of sp. gr. 0.810 was from 0.800 to 0.830. Oils of the same specific gravity and of the same grade were united and the products chilled and filtered to remove all the dissolved paraffine possible. The oils were chilled and filtered out of doors during the last of December when the thermometer stood at about 4° to 8° C. Lower temperatures would not only throw paraffine out of solution but would cause the whole oil to thicken as well. The oils were filtered through large plaited filters of drying paper, 24 hours or more often being required for a filter to empty completely. The lighter oils in grades A and B deposited no paraffine. The heavier grades deposited sometimes as much as 10 per cent of their weight, accompanied often by a slight change in specific gravity.

When these oils were filtered through earth again they behaved as shown in Table III. Nine hundred and fifty cc. were used in each tube, and for many tubes this amount of oil of the same grade (A, B, C, etc.) and of the same specific gravity was available. In some cases, however, it was necessary to unite oils of the same grade but which differed slightly in specific gravity. These differences never exceeded 0.0015. All cases in which this was done are marked *. The tube was divided into five sections. A, as before, is the top 8 cm., B the next 8, C the next 18, D the next 30, and EF the rest.

Table III.—The Second Fractionation.

	(20) A 0.8015		(21) A 0.806		(22)* B 0.805		(23) B 0.8055	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A	0.8012	36	0.8038	45	0.7997	50	0.8005	45
B	0.800	44	0.8035	48	0.802	50	0.8033	48
C	0.8012	68	0.8035	78	0.8055	108	0.805	115
	0.8027	35	0.8052	28				
D	0.8022	170	0.805	160	0.8063	175	0.8063	180
EF	0.8047	330	0.807	320	0.808	260	0.8085	260
		683		679		643		648

	(24) B 0.8065		(25) B 0.809		(26)* B 0.8105		(27)* B 0.812	
A	0.8077	38	0.8013	45	0.8075	38	0.8105	42
B	0.807	50	0.805	50	0.8085	50	0.8105	42
C	0.808	80	0.807	75	0.8105	100	0.8085	73
			0.810	30			0.810	22
D	0.8092	160	0.8095	180	0.8125	160	0.8115	140
EF	0.8115	300	0.8115	350	0.8135	275	0.8145	250
		628		730		523		569

	(28) C 0.8095		(29) C 0.810		(30) C 0.811		(31)* C 0.811	
A	0.805	52	0.8035	40	0.8005	50	0.803	50
B	0.8065	52	0.808	40	0.809	38	0.808	55
C	0.8085	70	0.810	75	0.812	115	0.813	105
	0.811	28	0.8115	30				
D	0.811	160	0.8115	140	0.813	175	0.8135	180
			0.8135	40				
EF	0.813	350	0.813	350	0.8145	310	0.8155	300
		712		715		688		690

Table III. (*Continued*).

	(32) C 0.8115		(33) C 0.813		(34)* C 0.8135		(35)* C 0.8135	
A	0.806	45	0.8072	20	0.803	42	0.8025	35
B	0.807	35	0.811	35	0.810	53	0.8077	35
C	0.810	60	0.812	70	0.813	100	0.8135	100
	0.812	33	0.813	25				
D	0.812	70	0.8145	90	0.815	150	0.8145	160
	0.813	97	0.815	80				
EF	0.813	103	0.8155	200	0.817	300	0.817	325
	0.8135	105	0.8155	125		645		655
	0.813	50	0.818	35				
	0.813	47		680				
	Unused,	63						
		708						

	(36) C 0.815		(37)* C 0.8155		(38)* C 0.8155		(39)* C 0.8165	
A	0.805	43	0.8053	50	0.808	40	0.808	50
B	0.8105	40	0.812	45	0.8095	50	0.8145	50
C	0.814	98	0.816	103	0.8135	100	0.816	82
D	0.815	155	0.8175	160	0.817	165	0.8175	125
EF	0.817	280	0.819	310	0.819	290	0.820	310
		616		668		645		617

	(40)* D 0.8135		(41) D 0.814		(42) D 0.814		(43) D 0.814	
A	0.8095	45	0.8045	30	0.806	32	0.806	25
B	0.8085	45	0.8115	45	0.811	45	0.8097	30
C	0.811	95	0.8135	75	0.813	92	0.814	50
			0.8165	28				
D	0.8155	165	0.818	140	0.8175	140	0.8157	145
EF	0.817	320	0.821	300	0.8195	310	0.8175	400
		670		618		619		650

Table III. (Continued).

	(44) D 0.814		(45) D 0.814		(46) D 0.8145		(47) D 0.815	
A	0.8008	45	0.800	50	0.808	45	0.800	42
B	0.8077	50	0.8065	55	0.8115	40	0.807	47
C	0.814	103	0.8125	100	0.8135	65	0.814	110
					0.8155	30		
D	0.8175	160	0.816	160	0.817	105	0.816	150
					0.818	58		
EF	0.819	310	0.817	300	0.8195	180	0.819	330
		668		665	0.8202	120		679
					0.821	53		
						696		

	(48) D 0.815		(49) D 0.8155		(50) D 0.8155		(51) D 0.8155	
A	0.810	37	0.8045	40	0.8105	45	0.8058	40
B	0.805	47	0.811	48	0.8148	47	0.810	40
C	0.812	105	0.815	98	0.810	100	0.8132	60
							0.8145	50
D	0.817	160	0.8185	160	0.815	140	0.8172	75
							0.8188	55
							0.8188	38
EF	0.819	300	0.820	310	0.819	400	0.820	38
		649		656		732	0.819	100
							0.8208	30
							0.8208	45
							0.8208	30
							0.8208	95
							Unused,	40
								736

	(52) D 0.816		(53)* D 0.816		(54) D 0.8165		(55) D 0.8165	
A	0.806	38	0.803	43	0.806	47	0.8095	42
B	0.8115	42	0.8105	30	0.811	48	0.8135	40
C	0.814	70	0.815	100	0.815	98	0.8145	77
	0.8175	25						
D	0.8185	125	0.8185	175	0.8188	150	0.8188	150
EF	0.821	300	0.820	290	0.8208	300	0.821	295
		700		638		643		604

Table III. (Continued).

	(56)* D 0.8165		(57)* D 0.817		(58)* D 0.818		(59) D 0.8187	
A	0.806	45	0.8075	40	0.808	45	0.811	40
B	0.810	45	0.8115	40	0.8135	45	0.812	45
C	0.8145	95	0.815	100	0.817	105	0.814	92
D	0.8185	160	0.818	130	0.820	150	0.819	150
EF	0.821	295	0.821	330	0.822	300	0.823	305
		640		640		645		623

	(60)* D 0.8205		(61)E 0.814		(62)* E 0.8163		(63)* E 0.817	
A	0.8045	45	0.8075	33	0.8155	42	0.804	45
B	0.813	45	0.810	35	0.808	50	0.8075	50
C	0.8175	90	0.8125	80	0.8095	70	0.8145	102
					0.812	25		
D	0.822	170	0.818	125	0.8175	105	0.8205	150
					0.8182	32		
EF	0.823	270	0.8245	300	0.823	250	0.8245	300
	Unused,	70			0.8255	41		
		692		573		615		647

	(64)* E 0.817		(65)* E 0.818		(66)* E 0.818		(67) E 0.818	
A	0.805	42	0.8065	90	0.805	38	0.805	40
			0.809	20				
B	0.810	42	0.810	110	0.811	38	0.811	45
C	0.8145	75	0.8155	186	0.8135	104	0.8145	85
			0.817	50				
D	0.820	135	0.8205	385	0.819	175	0.8185	125
			0.8205	75				
EF	0.8255	235	0.8255	650	0.8235	240	0.824	325
			0.8255	260				
		529		1826		695		620

3 tubes.

	(68)* E 0.8185		(69) E 0.819		(70) E 0.819		(71)* E 0.819	
A	0.8205	15	0.804	24	0.8115	21	0.8095	23
B	0.8043	35	0.808	40	0.814	31	0.8085	34
C	0.810	60	0.8145	85	0.815	90	0.814	80
	0.812	30						
D	0.817	160	0.8195	140	0.8165	120	0.820	160
EF	0.8225	300	0.824	300	0.824	330	0.824	280
		590		589		592		577

Table III. (Continued).

	(72)* E 0.8195		(73)* E 0.8195		(74) E 0.8195		(75) E 0.8197	
A	0.8145	30	0.8055	34	0.816	40	0.8025	40
B	0.8105	42	0.811	45	0.8135	42	0.8105	38
C	0.8135	103	0.8155	80	0.809	65	0.816	90
					0.814	34		
D	0.8195	160	0.820	120	0.8185	160	0.822	150
EF	0.824	285	0.824	290	0.824	260	0.8255	300
					0.827	30		
		620		569		631		618

	(76)* E 0.820		(77)* E 0.8205		(78) E 0.8215		(79)* E 0.822	
A	0.8045	48	0.806	32	0.8045	28	0.8105	32
B	0.812	40	0.8125	45	0.8135	36	0.8145	42
C	0.817	91	0.8175	90	0.8185	78	0.819	77
D	0.822	155	0.823	100	0.823	150	0.8225	155
EF	0.826	260	0.8245	330	0.8275	300	0.827	280
		594		597		592		586

	(80) E 0.822		(81) E 0.822		(82) E 0.824		(83)* A–B 0.804	
A	0.817	30	0.8083	26	0.8125	48	0.803	32
B	0.810	40	0.814	40	0.8127	48	0.8035	25
C	0.8153	46	0.8185	92	0.818	53	0.8035	63
	0.8163	42			0.819	50		
D	0.8225	160	0.824	140	0.8245	175	0.804	140
EF	0.8265	295	0.8265	270	0.828	200	0.806	275
					0.830	90		
		613		568	left,	50		535
						714		

	(84)* A–B 0.8065		(85)* A–B 0.808		(86)* B-C-D 0.8125		(87)* B-C-D 0.8125	
A	0.8035	40	0.8085	30	0.805	32	0.805	80
B	0.8055	40	0.807	30	0.808	42	0.8085	73
C	0.809	80	0.8065	92	0.813	85	0.812	118
							0.813	75
D	0.8085	155	0.8085	115	0.815	175	0.815	285
EF	0.811	300	0.8115	330	0.820	280	0.8175	520
		615		597		614		1151

2 tubes.

Table III. (*Continued*).

	(88)* C–D–E 0.813		(89)* C–D–E 0.813		(90)* B–C–D 0.8145		(91)* D–E 0.815	
A	0.8035	40	0.8035	130	0.8065	130	0.801	165
			0.807	20	0.808	27	0.8025	176
B	0.808	40	0.8077	160	0.809	137	0.8075	206
					0.8115	20	0.8085	156
C	0.8115	73	0.8125	330	0.813	305	0.812	330
	0.813	30	0.813	60	0.815	40	0.812	512
D	0.8155	160	0.815	550	0.815	560	0.817	340
			0.8175	90	0.8175	75	0.817	800
							0.817	150
EF	0.8195	290	0.8175	830	0.8175	775	0.8215	
		—	0.818	425	0.818	410	etc.	2733
		633		—		—		—
				2595		2479		5568
				4 tubes.		4 tubes.		9 tubes.

	(92*) D–E 0.8163		(93) F 0.822		(94) F 0.822	
A	0.805	84	0.8107	35	0.804	28
	0.8075	20				
B	0.807	100	0.810	43	0.808	37
	0.8115	20				
C	0.815	205	0.814	70	0.8165	63
	0.816	45	0.816	25	0.817	30
D	0.820	350	0.8215	156	0.8218	146
	0.820	102				
EF	0.8225	500	0.8285	250	0.831	255
	0.8225	480	0.831	60		—
		—		—		559
		1906		639		

To chill and filter these products of two fractionations would have entailed too much loss. As it was, much uniting of samples which differed but slightly from one another was necessary to obtain sufficient oil for further fractionation. The unions which were made are given in Table IV.

Table IV.—Products of Two Fractionations United for the Third Fractionation.

Lot.	Sp. gr.	Grade.	Fractions united: Sp. gr.	cc.	Grade.	Sp. gr.	cc.	Grade.	Sp. gr.	cc.			
95	0.805	B	0.8033	48	A	0.8035	240	B	0.8035	25			
		C	0.8035	63	A	0.804	65	D	0.804	140			
		A	0.8045	150	A	0.805	360	B	0.805	95			
		C	0.805	115									
96	0.807	A	0.8058	40	A	0.806	235	EF	0.806	275			
		A	0.8065	240	B	0.8065	100	D	0.8063	180			
		A	0.807	53	C	0.807	75	C	0.8065	92			
97	0.8085	B	0.808	767	C	0.808	80	A	0.8083	26			
		A	0.809	20	C	0.809	210	A	0.8085	118			
98	0.8085	A	0.8072	20	A	0.8075	290	B	0.8075	480	D	0.8075	270
		A	0.8077	38									
99	0.8105	A	0.8105	70	C	0.8105	270	A	0.811	40	B	0.811	580
		C	0.811	115	A	0.8115	21	B	0.8115	308	C	0.8115	73
100	0.8115	EF	0.811	300	EF	0.8115	920						
101	0.8125	C	0.8123	520	D	0.8125	160	EF	0.8125	820			
102	0.813	C	No uniting necessary.										
103	0.8135	B	0.8125	180	B	0.813	45	C	0.8132	60			
		B	0.8135	106	C	0.8135	925						
104	0.814	D	0.8135	370	EF	0.8135	715						
105	0.814	C	No uniting necessary.										
106	098145	D	0.814	500	C	0.8145	910						
107	0.815	D	No uniting necessary.										
108	0.8155	EF	"	"	"								
109	0.8163	D	"	"	"								

Table IV. (*Continued*).

110	0.817	D	No uniting necessary.								
111	0.817	EF	"	"	"						
112	0.8175	C	0.8165	258	D	0.817	425	D	0.8172	75	
		C	0.8175	200							
113	0.8175	EF	No uniting necessary.								
114	0.8187	EF	"	"	"						
115	0.819	D	0.8175	305	D	0.818	990				
116	0.819	EF	0.8185	845	EF	0.819	683				
117	0.819	D	No uniting necessary.								
118	0.819	EF	"	"	"						
119	0.8195	EF	"	"	"						
120	0.820	D	0.8195	475	D	0.820	600				
121	0.821	EF	No uniting necessary.								
122	0.8215	EF	"	"	"						
123	0.822	EF	0.8215	700	D	0.8218	460	EF	0.822	300	
124	0.8225	EF	No uniting necessary.								
125	0.8235	EF	"	"	"						
126	0.824	D	0.823	250	EF	0.8235	860	D	0.824	140	
127	0.8255	EF	No uniting necessary.								

Nine hundred and fifty cc. of each of these were fractionated by earth again, with the results given in Table V.

Table V.—The Third Fractionation.

	(95) A–D 0.805		(96) A–EF 0.807		(97) A–C 0.8085		(98) A–D 0.8085	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A	0.8065	33	0.8045	37	0.806	40	0.8047	38
B	0.805	33	0.806	38	0.8068	40	0.8052	38
C	0.804	62	0.8065	65	0.807	58	0.808	70
	0.805	40	0.8083	25	0.8095	18	0.8093	30
D	0.8055	150	0.808	142	0.8093	154	0.8095	132
EF	0.808	315	0.8095	250	0.812	295	0.811	335
		633		557		605		643

	(99) A–C 0.8105		(100) EF 0.8115		(101) C–EF 0.8125		(102) C 0.813	
A	0.8105	33	0.8065	30	0.808	33	0.806	26
B	0.810	36	0.809	36	0.8085	34	0.8105	33
C	0.8075	71	0.810	60	0.811	54	0.8105	50
	0.8085	17	0.812	20	0.8145	22	0.813	17
D	0.811	115	0.812	136	0.8145	162	0.813	136
EF	0.814	300	0.815	315	0.817	295	0.8157	365
		572		597		600		627

	(103) B–C 0.8135		(104) D–EF 0.814		(105) C 0.814		(106) C–D 0.8145	
A	0.8065	28	0.8042	35	0.804	40	0.803	33
B	0.810	33	0.8115	36	0.810	40	0.810	40
C	0.8135	60	0.8125	60	0.8142	58	0.8145	54
	0.8165	18	0.8147	28	0.816	25	0.816	22
D	0.815	150	0.815	175	0.8163	270	0.816	150
EF	0.817	325	0.819	230	0.8185	280	0.8185	260
		614		564		713		559

Table V. (*Continued*).

	(107) D 0.815		(108) EF 0.8155		(109) D 0.8163		(110) D 0.817	
A	0.8035	45	0.809	52	0.810	33	0.8065	35
B	0.8115	47	0.811	47	0.8105	45	0.8125	40
C	0.815	85	0.815	55	0.8132	55	0.817	68
	0.8177	30	0.815	40	0.8145	33	0.818	30
D	0.8175	156	0.8165	170	0.8185	140	0.8195	145
EF	0.8195	300	0.8185	255	0.8215	275	0.821	290
		663		619		581		608

	(111) EF 0.817		(112) C–D 0.8175		(113) EF 0.8175		(114) EF 0.8187	
A	0.8043	30	0.8145	35	0.8065	35	0.817	30
B	0.8105	32	0.811	32	0.812	48	0.8065	25
C	0.8152	65	0.8165	60	0.8155	75	0.8122	30
	0.816	43	0.818	30	0.8175	18	0.813	15
D	0.8182	160	0.819	150	0.8185	150	0.8175	150
EF	0.8205	290	0.822	245	0.8225	283	0.822	340
		620		552		609		590

	(115) D 0.819		(116) EF 0.819		(117) D 0.819		(118) EF 0.819	
A	0.8055	16	0.8032	30	0.8045	33	0.805	30
B	0.807	lost	0.8115	36	0.813	38	0.813	30
C	0.816	43	0.816	52	0.8175	60	0.8165	60
	0.817	30	0.820	21	0.8175	34		10
D	0.820	130	0.8205	160	0.8215	150	0.821	154
EF	0.8225	300	0.8235	240	0.8235	325	0.8243	295
		lost		539		640		579

Table V. (Continued).

	(119) EF 0.8195		(120) D 0.820		(121) EF 0.821		(122) EF 0.8215	
A	0.805	23	0.805	33	0.8075	33	0.803	41
B	0.814	35	0.811	35	0.814	41	0.811	43
C	0.8165	58	0.817	53	0.8182	63	0.8165	60
	0.8175	32	0.8175	35	0.819	18	0.818	23
D	0.8205	152	0.822	165	0.822	150	0.8225	182
EF	0.823	300	0.825	310	0.8245	273	0.828	270
		600		633		578		629

	(123) D–EF 0.822		(124) EF 0.8225		(125) EF 0.8235		(126) D–EF 0.824	
A	0.808	34	0.807	31	0.804	35	0.805	35
B	0.813	35	0.8095	27	0.813	40	0.814	35
C	0.8178	52	0.8175	65	0.8185	70	0.820	60
	0.8192	42	0.8185	17	0.8195	21	0.821	20
D	0.8233	155	0.8232	150	0.8252	144	0.8253	170
EF	0.8265	260	0.8275	300	0.829	280	0.828	300
		578		590		590		620

	(127) EF 0.8255	
A	0.8055	45
B	0.8155	40
C	0.821	75
	0.823	25
D	0.8275	170
EF	0.830	280
		635

From the products of the third fractionation, oil of five grades was obtained in sufficient quantity by uniting fractions as given in Table VI., the results of the fourth fractionation being given in Table VII.

Table VI.—Products of Three Fractionations United for the Fourth Fractionation.

Lot.	Sp. gr.	Composed of				Composed of			
128	0.815	(99)	EF	0.814	300 cc.	(100)	EF	0.815	315 cc.
		(101)	C	0.8145	22 "	(101)	D	0.8145	162 "
		(103)	D	0.815	150 "	(104)	C	0.8147	28 "
		(104)	D	0.815	175 "	(105)	C	0.8142	58 "
		(106)	C	0.8145	54 "	(107)	C	0.815	85 "
		(108)	C	0.815	55 "	(108)	C	0.815	40 "
		(109)	C	0.8145	33 "	(111)	C	0.8152	65 "
									1542
129	0.8168	(101)	EF	0.817	295 cc.	(105)	D	0.8163	270 cc.
		(102)	EF	0.8157	365 "	(106)	D	0.816	150 "
		(103)	EF	0.817	325 "	(108)	D	0.8165	170 "
									1575
130	0.819	(104)	EF	0.819	230 cc.	(108)	EF	0.8185	255 cc.
		(105)	EF	0.8185	280 "	(113)	D	0.8185	150 "
		(106)	EF	0.8185	260 "	(109)	D	0.8185	140 "
									1315
131	0.8205	(107)	EF	0.8195	300 cc.	(115)	D	0.820	130 cc.
		(110)	D	0.8195	145 "	(116)	D	0.8205	160 "
		(111)	EF	0.8205	290 "	(118)	D	0.821	154 "
		(119)	EF	0.8205	152 "				1467
132	0.823	(113)	EF	0.8225	283 cc.	(120)	D	0.822	165 cc.
		(115)	EF	0.8225	300 "	(121)	D	0.822	150 "
		(119)	EF	0.823	300 "	(122)	D	0.8225	182 "
									1380

Table VII.—The Fourth Fractionation.

	(128) C–EF 0.815		(129) D–EF 0.8168		(130) D–EF 0.819		(131) D–EF 0.8205	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A	0.8135	19	0.812	30	0.8115	24	0.8095	18
B	0.815	27	0.8122	42	0.8127	35	0.813	26
C	0.8118	50	0.8165	55	0.8173	60	0.819	45
	0.813	15	0.818	25	0.8185	22	0.8195	17
D	0.8147	140	0.818	160	0.820	160	0.8215	130
EF	0.8175	360	0.8195	305	0.8215	310	0.824	340
		611		617		611		576

	(132) D–EF 0.823	
	Sp. gr.	cc.
A	0.8092	35
B	lost	35
C	0.8195	60
	0.8213	25
D	0.8235	150
EF	0.826	280
		585

To better compare the oils of different specific gravities which were obtained by the process just described five samples of 300 cc. each were separated, by distillation, into ten fractions. Each was distilled in the same 500 cc. distilling bulb, which was heated by an electric stove entirely surrounding the bulb. Each was first heated to 200° under atmospheric pressure and then to 360° under 50 mm. pressure. The diminished pressure was obtained by means of a large Chapman water pump and kept constant at 50 mm. by the use of a valve which automatically admitted air to the evacuated system whenever the pressure fell below 50 mm.

This valve was constructed from a piece of iron pipe one inch in diameter and five feet long. The lower end was closed with a cap and the pipe filled with mercury to a depth of 76 cm. The upper end of the pipe was closed with a two-hole rubber stopper. In one hole was a long glass tube,

with the lower end beveled, which reached to the bottom of the mercury and which could be raised or lowered as the barometer varied from day to day. In the other hole of the stopper was a tube which passed just through the stopper and which was connected on the outside with the apparatus to be exhausted. To prevent mercury from being drawn up and over into the apparatus by the air admitted, the end of the tube inside the stopper was drawn out and bent at a right angle and over this was slipped a cap made of larger tubing which was closed at the bottom but which had a fine opening in the side for air. This cap was about six cm. long and extended about three cm. below the end of the tube inside. If any mercury passed through this first fine opening into the cap, it would fall to the bottom without being drawn over into the apparatus or clogging the fine opening in the tube leading to it. With this valve there was no difficulty in keeping a pressure of 50 mm. constant to within one mm.

The specific gravity, viscosity, and percentage absorbed when treated with concentrated sulphuric acid (sp. gr. 1.84), of each distillate of sufficient volume, which was not too viscous or partly solid, was determined.

Viscosity was measured by taking the time of flow of a measured volume of oil through a capillary, the viscometer used being the one described by Ostwald and Luther and modified by Jones and Veazey.[1] The capacity of the small bulb was 4.5 cc. and the diameter of the capillary such as to require from five to eight minutes for that amount of oil to flow through it, and 1 minute 2.6 seconds for the same amount of water. The viscosity as well as specific gravity was always measured at 20°.

Viscosities have been calculated from the following formula: $\eta = \eta_0 \frac{TS}{T_0 S_0}$, in which η_0 is the coefficient of viscosity for water, S_0 is the specific gravity of water, and T_0 the time of flow of water through any given capillary at a given temperature; η is the viscosity coefficient of the solution investigated, S is its specific gravity as compared with water as

[1] Z. physik. Chem., **61**, 651.

unity at any given temperature, and T is the time of flow of the given solution at that temperature. The value for pure water at 20° was taken from the work of Thorpe and Rodger.[1]

Thirty cc. of each of these distillates, where that much oil was available, or the whole of the fraction when it was not equal to 30 cc., were mixed with an equal volume of concentrated sulphuric acid (sp. gr. 1.84) and shaken half an hour or longer in a shaking machine. The oil and acid were then poured into a separating funnel and the acid drawn off. The oil was then washed twice with water, once with aqueous sodium hydroxide, again with water, and then with this last wash water poured into a burette and allowed to settle. After standing overnight the volume was read.

The oils boiling below 200° (50 mm.) separated clear, but the heavy distillates were milky from water. The volume of these milky oils was read, their specific gravity determined, and then the milkiness was removed by shaking and heating to 60° or so with calcium chloride. The specific gravity of the clear oil was then measured and the proper correction applied to the volume of the milky oil. In no case, however, was this correction at all large, and only for the three or four heaviest oils did it exceed one-half of 1 per cent, the largest correction of all being 2.6 per cent for the distillate between 230°–260° of the oil of sp. gr. 0.824. An attempt to treat with acid the oils selected for distillation resulted in so much loss from the formation of emulsions that the loss in volume and change in specific gravity could not be determined with any degree of accuracy.

[1] Phil. Trans. [A], **185**, 397 (1894).

Table VIII.—Degree of Fractionation Obtained by Distillation.

		(1)	(2)	(3)	(4)	(5)	(6)
	Sp. gr.	0.801	0.808	0.815	0.8195	0.824	0.810
	Viscosity	0.0404	0.0555	0.0589		0.0657	0.0441
	Tubes passed through	1	3	3	4	4	crude oil
Normal pressure below 150°	cc	36	1	13.	5	2	45.
	Sp. gr	0.720		0.737			0.714
	Viscosity	0.0052		0.0059			0.0047
	Acid treatment: Per cent abs	4.4		...			8.6
	Acid treatment: Sp. gr	0.722		0.7365			0.712
150°–200°	cc	47	61	52	60	60	43
	Sp. gr	0.749	0.7465	0.756	0.757	0.759	0.759
	Viscosity	0.0075	0.0073	0.0075	0.0073	0.0072	0.0076
	Acid treatment: Per cent abs	3.4	4.4	8.2	11.3	12.0	9.3
	Acid treatment: Sp. gr	0.749	0.7469	0.750	0.749	0.750	0.752
50 mm. pressure below 140°	cc	10	9	3	6	10	19
	Sp. gr						0.7805
	Viscosity						0.0112
	Acid treatment: Per cent abs						11.9
	Acid treatment: Sp. gr						0.7735

Table VIII. (Continued).

			(1)	(2)	(3)	(4)	(5)	(6)
140°–200°	cc.		69	75	80	80	73	48
	Sp. gr.		0.790	0.790	0.797	0.800	0.8015	0.804
	Viscosity		0.0212	0.0185	0.0211	0.0216	0.0196	0.0254
	Acid treatment	Per cent abs.	3.4	4.4	8.9	9.6	14.8	11.0
		Sp. gr.	0.790	0.7885	0.7915	0.795	0.7915	0.799
200°–230°	cc.		25	30	23	25	30	21
	Sp. gr.		0.813	0.8135	0.818	0.8225	0.822	0.823
	Viscosity		0.0556	0.0594	0.0573	0.0661	0.0505	0.0593
	Acid treatment	Per cent abs.		4.3	11.0	8.4	10.5	8.7
		Sp. gr.	0.813	0.8125	0.816	0.8217	0.818	0.8175
230°–260°	cc.		23	27	23	20	24	22
	Sp. gr.		0.8255	0.826	0.830	0.833	0.838	0.8355
	Viscosity		0.1106	0.1150	0.1116	0.1168	0.1259	0.1248
	Acid treatment	Per cent abs.	3.4	8.5	7.0	8.8	7.6	12.6
		Sp. gr.	0.8255	0.8255	0.828	0.832	0.833	0.830

Table VIII. (*Continued*).

260°–300°	cc.	20	22	23	24	20	17
	Sp. gr.	0.8395	0.838				
	Viscosity	0.2520		fluid	fluid	fluid	fluid
300°–340°	cc.	25	30	27	30	26	25
	Sp. gr.	0.847	0.849	solid	solid	solid	solid
340°–360°	cc.	21 fluid	26 fluid	(below 355°) fluid	22	19 fluid	20 fluid
Residue	cc.	22 fluid	17 fluid	30 fluid	45 fluid	35 fluid	32 fluid
Total volume		298	298	296	295	299	292

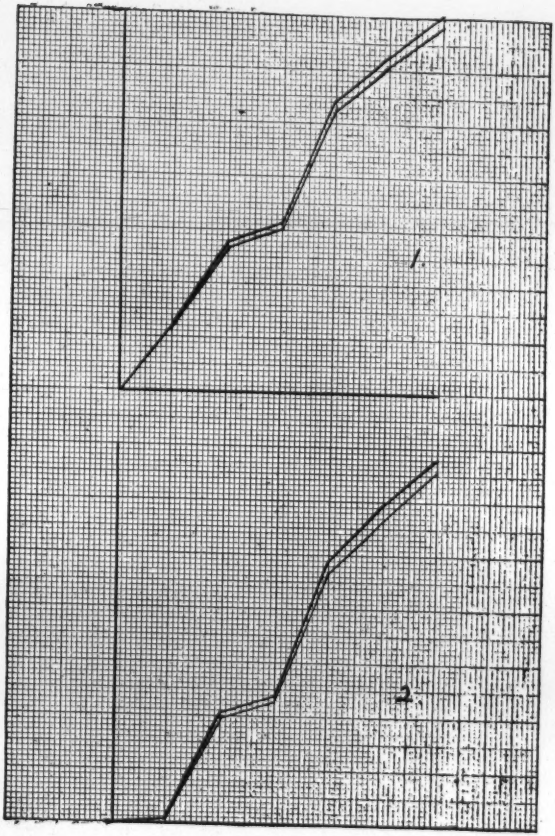
By "fluid" in the above table is meant that the oil at 20° was partly solid but would flow when the bottle was inclined; by "solid," that the bottle could be turned upside down without the oil changing shape.

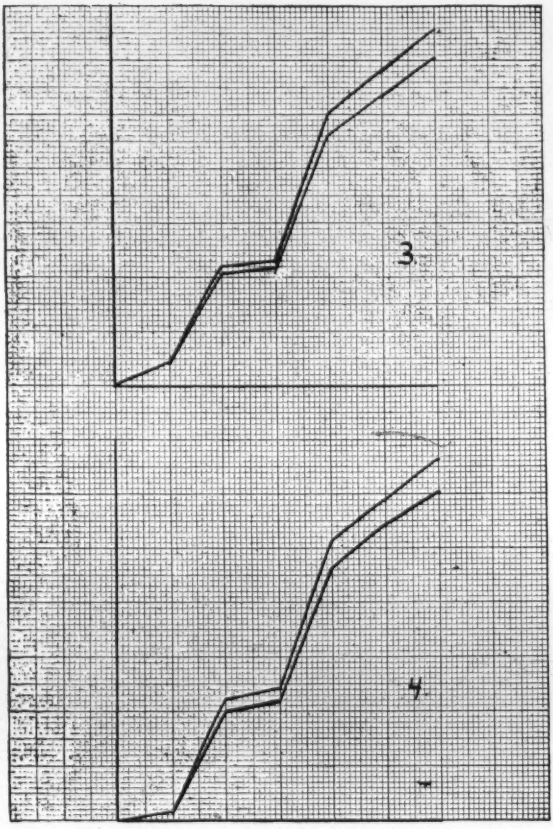
It was hoped that sulphuric acid of the strength used (sp. gr. 1.84) would dissolve only unsaturated hydrocarbons and leave untouched the paraffines and benzene. By long-continued shaking at ordinary temperature, however, benzene is dissolved by acid of this strength, provided that the acid is in large excess. One hundred cc. of benzene were completely dissolved in 434 cc. of acid on being shaken four hours.

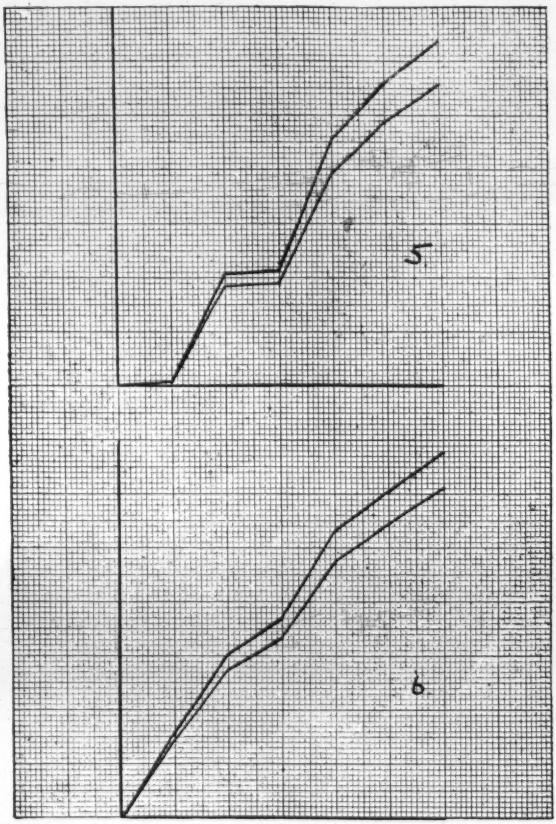
Three of the distillates which had been shaken with acid, however, gave no action when treated with a mixture of equal parts concentrated sulphuric acid and fuming nitric acid, while distillates which had not been previously shaken with sulphuric acid were acted upon by this nitrating mixture. The action of the sulphuric acid, therefore, appears to have been complete.

The action of sulphuric acid shows that over 90 per cent of the oil dealt with consists of paraffine hydrocarbons, and that in the filtration through earth the paraffine hydrocarbons tend to collect at the top of the tube and the unsaturated hydrocarbons at the bottom.

The increasing amount dissolved by sulphuric acid in the heavier oils may be seen in the following curves. The abscissas represent temperatures and the ordinates volumes. The same distance upon the X axis is taken to represent a distillate, regardless of the number of degrees over which it may have been collected. The upper curve represents the percentage of the total volume which distilled between given temperatures; the lower curve, the percentage of the total volume recovered which was not absorbed by sulphuric acid (*i. e.*, the paraffine hydrocarbons). For the upper curve the ordinates were obtained by dividing the number of cubic centimeters in the distillate by the total volume of oil recovered. For the lower curve the ordinates were obtained by dividing the number of cubic centimeters in the distillate not absorbed by sulphuric acid by the total volume of oil recovered.


Volume.
1.
Volume.
2.
Temp. 0° 150° 200° 140° 200° 230° 260°
Normal pressure.
50 mm. pressure.


Volume.
3
Volume.
4
Temp. 0° 150° 200° 140° 200° 230° 260°
Normal pressure.
50 mm. pressure.


Volume.
5
Volume.
6
Temp. 0° 150° 200° 140° 200° 230° 260°
Normal pressure.
50 mm. pressure.

The area between the two curves represents the proportion of hydrocarbons soluble in sulphuric acid. This, it will be seen, is greatest for the oils of highest specific gravity.

On referring to Tables III. and V. it will be noticed that for several tubes the oil of grade A is heavier than that of grade B and sometimes of grade C. Tubes where this irregularity is marked are 48, 62, 68, 72, 74, and 80 of Table III., and 112 and 114 of Table V. A slight irregularity appears in 20, 21, 24, 27, 40, 71, and 85 of Table III. and in 99 of Table V. Where the oils in these cases are not colorless, the color is strongest in those whose specific gravity is greatest, so that although oil of the grade A has passed through the most earth it is yet more strongly colored than oil of grade B or C.

No reason for this variation has been established. It should be remembered, however, that the different oils rise in the earth with differing velocities, not because they differ from one another in specific gravity but because they differ in surface tension. A rough attempt was made to measure relative surface tensions by measuring the height to which different oils rise in the same capillary tube, but although a cathetometer was used and the level of the oil in the capillary brought to the same spot each time, the work sufficed only to show that the difference between the surface tension of the oils obtained was so slight as to require very careful measurement for the results to be of any value.

That viscosity shows the same irregularity as color and specific gravity in these oils appears from the the following measurements.

	(62)		(68)	
	Sp. gr.	Vis.	Sp. gr.	Vis.
A	0.8155	0.0539	0.8205	0.0626
B	0.808	0.0469	0.8043	0.0469
C	0.8095	0.0509	0.810	0.0520
	0.812	0.0555	0.812	0.0554
D	0.8175	0.0525	0.817	0.0524
	0.8182	0.0535		
EF	0.823	0.0612	0.8225	0.0606

In (50) of Table III. an irregularity appears in grade B which is also found in the viscosity.

	(50)	
	Sp. gr.	Vis.
A	0.8105	0.0532
B	0.8148	0.0559
C	0.810	0.0526
D	0.815	0.0526
EF	0.819	0.0552

The oils obtained by one fractionation of the crude petroleum have the following viscosities, the fractions measured being those previously given in Table I.

	(1)		(2)		(3)	
	Sp. gr.	Vis.	Sp. gr.	Vis.	Sp. gr.	Vis.
A	0.796	0.0376	0.8012	0.0408	0.8022	0.0401
B	0.808	0.0529	0.804	0.0485	0.803	0.0470
C	0.8125	0.0501	0.807	0.0443	0.8075	0.0453
	0.8137	0.0529	0.809	0.0476	0.810	0.0471
D	0.815	0.0504	0.8125	0.0460	0.812	0.0472
E	0.818	0.0521	0.8185	0.0537	0.8175	0.0529
F	0.8205	..	0.823	..	0.821	..

That the viscosity does not increase with the specific gravity, particularly with the higher fractions, is apparent in two of the three series just given. The same is also shown in the following four samples taken from Table III.

	(21)		(22)	
	Sp. gr.	Vis.	Sp. gr.	Vis.
A	0.8038	0.0465	0.7997	0.0421
B	0.8035	0.0456	0.802	0.0485
C	0.8035	0.0456	0.8055	0.0502
	0.8052	0.0485		
D	0.805	0.0479	0.8063	0.0496
EF	0.807	0.0480	0.808	0.0510

	(47)		(53)	
	Sp. gr.	Vis.	Sp. gr.	Vis.
A	0.800	0.0453	0.803	0.0515
B	0.807	0.0538	0.8105	0.0563
C	0.814	0.0542	0.815	0.0684
D	0.816	0.0528	0.8185	0.0570
EF	0.819	0.0556	0.820	0.0559

This decrease of viscosity in the oils at the bottom of the tube appears to be a regular phenomenon in the dozen or so oils which have been tested. This point will be investigated further.

Water Fractionation.

To test the effectiveness of water fractionation alone, 1000 cc. of crude petroleum, previously chilled and filtered, of specific gravity 0.807, were mixed with 1000 grams of earth and allowed to stand 24 hours. Water was then added in small amounts and the oil collected.

	Sp. gr.	Volume of oil. cc.	Total water present. cc.
A	0.8148	44	500
B	0.8139	278	650
C	0.816	211	800
D	0.820	84	950
E	0.8225	28	1400
F	0.8245	28	2750
		673	

The fractions of large enough volume were then mixed with earth again and the oil replaced with water. One gram of earth was used for each cc. of oil, the earth first having been heated and allowed to cool.

B. 0.8139 278 cc. Stood 1.5 hours.			C. 0.816 211 cc. Stood 6 hours.			D. 0.820 84 cc. Stood 2.5 hours.		
Sp. gr.	Oil.	Water. cc.	Sp. gr.	Oil.	Water. cc.	Sp. gr.	Oil.	Water. cc.
0.8185	10	70	0.820	10	80	0.822	32	76
0.818	10	110	0.820	20	125	0.823	20	207
0.818	21	164	0.8195	72	250		—	
0.818	20	..	0.820	30	410		32	
0.817	42	..	0.820	10	588			
0.819	10	216		—				
0.820	44	277		142				
0.820	16	428						
0.8215	20	686						
	—							
	193							

It is apparent that while petroleum is fractionated by simply mixing the oil with fuller's earth and then displacing the oil from the earth with water, the fractionation is much less complete than when tubes are used, as previously described.

It will be noticed that although fractions C and D in the table last given are hardly separated at all by further treatment with earth and water, yet the specific gravity of all the oil recovered is higher than that of the oil used, *e. g.*, from C of sp. gr. 0.816 is obtained nothing lighter than 0.8195, and from D of sp. gr. 0.820 nothing lighter than 0.822.

To determine whether the specific gravity of the oil recovered will continue to rise after the oil is fractionated no further by repeated treatment, 330 cc. of sp. gr. 0.819, obtained by uniting several products of one fractionation of the crude petroleum, were mixed with 330 grams of earth and water was added.

	Sp. gr.	Vol. oil.	Total water present. cc.
A	..	6	64
B	0.8215	50	...
C	..	12	214
D	0.821	60	270
E	0.821	82	413
F	0.8225	26	613
		236	

Seventy-five cc. of E of sp. gr. 0.821 were next mixed with 75 grams of earth and 150 cc. of water were added. Fifty-one cc. of oil whose specific gravity was unchanged, but whose color was decreased, were obtained. Fifty cc. of this, when treated with earth and water, yielded 34 cc. of oil of considerably lighter color, but whose specific gravity was still 0.821.

Although only two-thirds of the oil used is recovered whenever oil is mixed with earth and then displaced with water, yet this loss does not seem to affect the specific gravity of the oil obtained for more than one or two treatments after the oil ceases to be fractionated. After this the oil recovered has the same specific gravity as the oil used.

The Oil Lost in the Earth.

The sum of the fractions of oil displaced from the earth is usually about two-thirds of the volume of the oil used.

A pressure of approximately 200 tons per square inch upon the earth from which water has displaced all the oil that it can results in the liberation of considerable water but very little oil. When earth which has been pressed is heated to 165° for three hours, considerable water distils over but much less oil than would be expected, *e. g.*, from 75 grams of earth which should contain 25 cc. of oil, but 4 cc. of oil were obtained. The earth was removed once from the flask and pulverized, and when the heat was discontinued the earth was thoroughly dry. On extraction with ether the earth gave a solution having the color of the original petroleum. The extraction was made with a Soxhlet extractor and continued until the extract was colorless. On evaporation of the ether there remained about 8 cc. of a heavy oil with the color of the natural petroleum. Pressure, heat, and extraction with ether together gave about half the amount of oil which the earth must have contained.

Earth which had been used once was allowed to dry for several weeks at room temperatures until it had lost all appearance of containing moisture. It was then pulverized, sifted, and used in a tube with the crude petroleum of sp. gr. 0.810 with the following results:

		cc.
8 cm. at top	..	0
Next 8 cm	0.8284	10
Next 18 cm	0.8225	45
Next 30 cm	0.8143	60
	0.8155	80
Rest	0.8175	83
	0.819	114
		392 cc.

Earth used, 720 grams.
Crude petroleum used, 740 cc.

The first oil up the tube evidently is absorbed by heavy material in the earth, while the first oil recovered dissolves

material from the earth, which increases its specific gravity beyond that of the next fraction.

To see how much of the weight of the earth just used was due to material which it had retained from its first use, 300 grams of earth were mixed with 300 cc. of crude petroleum and the oil displaced by water. The oil recovered measured 205 cc., and the weight of the earth after drying for several weeks at room temperature was 347.5 grams. Fully 15 per cent, therefore, of the weight of the earth used in the tube just mentioned was solid matter which it had retained from its first use.

In all cases the earth was heated before it was used because it was believed that heating decreased the amount of oil lost in the earth. The earth was heated usually in iron pans on a gas stove until it ceased to form geysers when stirred. A tube packed with earth which had not been heated gave the following results with crude petroleum of sp. gr. 0.810.

	Sp. gr.	Vol. cc.
Top 8 cm	0.803	30
Next 8 cm	0.8045	38
Next 18 cm	0.8103	85
Rest	..	440
		593
Crude oil used		930

Earth used, 948 grams.
Tube 5 feet long, $1^1/_4$ inches diameter.
20 hours required at diminished pressure.

In a case of water fractionation alone with unheated earth but 242 cc. of oil were recovered from 500 cc. of crude petroleum.

Results obtained toward the close of our work indicate that the loss of oil when unheated earth is used is much less than we had supposed it to be. The gain from heating the earth may not pay for the trouble of doing so, and this point should be investigated before any very extensive investigation is again undertaken.

Earth after heating must become thoroughly cold before it is used to pack tubes. The earth holds its heat for several

hours, and if it is used the same day upon which it is heated, there is apt to be contraction sufficient to allow the oil to run up the side of the tube as it would in a vacuum.

The length of the tubes used was five and one-half feet. A tube nine feet long was kept for two days with a constant diminished pressure of about 10 cm. mercury, and connected to the same vacuum pump with several five and one-half foot tubes. The oil was drawn to the top of the latter, which were removed and a second lot substituted. When these were likewise fully impregnated with oil the long tube was opened. The oil had ascended but 45 cm., showing that the diminished pressure had not penetrated that length of earth and reached the bottom of the tube.

A shorter tube in which the earth was packed very much harder, so that the tube filled with earth rang like an iron rod when pounded upon the floor, was connected with a vacuum pump at one end and a manometer at the other. Diminished pressure was indicated by the manometer when the column of earth was two feet long but not when it was two feet four inches.

The Fractionating Power of Substances Other than Fuller's Earth.

A clay from Topsham, Maine, was found which in tubes showed a power of fractionating as well as decolorizing the higher fractions. Compared with fuller's earth, the action was as follows.

	Sp. gr.	
	Clay.	Fuller's earth.
8 cm. at top.....	0.799	0.793
Next 8 cm.....	0.804	0.800
Next 8 cm.....	0.810	0.806
Next 10 cm.....	0.810	0.807
Next 30 cm.....	0.812	0.8092
Next 45 cm.....	0.812	0.8112
Time required,.....	69 hours,	76 hours.
Sp. gr petroleum used,	0.806.	

Tubes 5 feet long, $1^1/_4$ inches in diameter.

Neither powdered brick made from the same clay nor powdered feldspar showed any power of fractionation.

Another similar clay (from Mere Point, Brunswick, Maine) showed a power of water fractionation, but its behavior in a tube was not tested. Four hundred grams of this clay, previously sifted and heated, were mixed with 170 cc. of crude petroleum of sp. gr. 0.806 and allowed to stand 14 hours. Water was then added and the following fractions obtained:

Sp. gr.	Vol. in cc.	Total water present.
0.8165	24	104
0.817	60	133
0.8188	20	234
..	6	374
	110	

The color was scarcely changed at all.

Summary.

(1) When petroleum is allowed to rise in a tube packed with fuller's earth, there is a decided fractionation of the oil, the fraction at the top of the tube being of lower specific gravity than that at the bottom.

(2) When water is added to fuller's earth which contains petroleum, the oil which is displaced first differs in specific gravity from that which is displaced afterwards when more water is added.

(3) When petroleum is allowed to rise in a tube packed with fuller's earth, the paraffine hydrocarbons tend to collect in the lightest fraction at the top of the tube and the unsaturated hydrocarbons at the bottom.

(4) Whenever oil is mixed with fuller's earth and then displaced with water, about one-third of the oil remains in the earth.

This work will be continued in this laboratory, using a variety of oils and also studying a number of questions which have presented themselves.

JOHNS HOPKINS UNIVERSITY,
June, 1908.

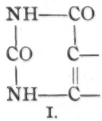
[Contributions from the Sheffield Laboratory of Yale University.]

CLXIII.—RESEARCHES ON PYRIMIDINES: SYNTHESES OF NEW DERIVATIVES OF 5-HYDROXY-URACIL (ISOBARBITURIC ACID).

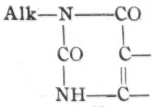
[THIRTY-NINTH PAPER.]

By Treat B. Johnson and D. Breese Jones.

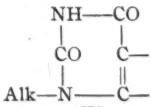
Johnson and Clapp[1] have shown that 1- and 3-alkyl derivatives of 2,6-dioxytetrahydropyrimidines, I., can be distinguished by the difference in their behavior towards diazobenzenesulphonic acid. The 1-alkylpyrimidines, II., react with the sulphonic acid, in presence of alkali, giving red colored solutions, while the isomeric 3-alkylpyrimidines, III., do not give red colors under the same conditions. This interesting behavior of 1-alkylpyrimidines enabled Johnson and Derby[2] to determine the structures of the isomeric 1- and 3-benzyl derivatives of uracil and thymine.



I.

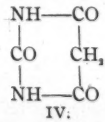


II.

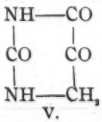


III.

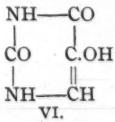
We have also found this diazo reagent to be of service for determining the structures of some new 1- and 3-alkyl derivatives of isobarbituric acid. The name—isobarbituric—signifies a compound isomeric with barbituric acid, IV., and having the constitution of a hexahydropyrimidine, as represented by formula V. The reactions of this pyrimidine, however, do not indicate a hexahydro compound but rather a tetrahydropyrimidine, as represented by formula VI., *viz.*, *5-hydroxyuracil.*



IV.



V.



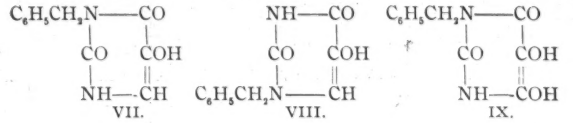
VI.

[1] J. Biol. Chem., **5**, 163 (1908).

[2] This Journal, **40**, 444 (1908).

Formula VI. is supported by the facts that the pyrimidine does not give an oxime[1] and also that the hydrogen of the 5-hydroxyl group is replaceable by the acetyl radical[2] when the pyrimidine is warmed with acetic anhydride. Furthermore, the pyrimidine and its ethyl ether[3] react with diazobenzenesulphonic acid, giving red colors as intense as that obtained with thymine.[4]

We shall describe in this paper the preparation and properties of 1-benzyl-5-hydroxyuracil (1-benzylisobarbituric acid), VII., 3-benzyl-5-hydroxyuracil (3-benzylisobarbituric acid), VIII., and also 1-benzylisodialuric acid, IX.



VII. VIII. IX.

Johnson and McCollum[5] have shown that pseudoethylthiourea condenses smoothly with the sodium salt of ethyl α-ethoxy-β-oxyacrylate, giving 2-ethylmercapto-5-ethoxy-6-oxypyrimidine, X. This mercaptopyrimidine reacted with benzyl chloride, in presence of alkali, giving two isomeric pyrimidines, *viz.*, 1-benzyl-2-ethylmercapto-5-ethoxy-6-oxypyrimidine, XII., melting at 140°–141°, and 2-ethylmercapto-3-benzyl-5-ethoxy-6-oxypyrimidine, XIII., melting at 85°–86°. We did not observe the formation of 2-ethylmercapto-5-ethoxy-6-benzoxypyrimidine, XI. These two mercaptobenzylpyrimidines, XII. and XIII., were converted smoothly by hydrolysis with hydrochloric and hydrobromic acids into 1-benzyl-5-hydroxyuracil, XVII., melting at 230°, and 3-benzyl-5-hyroxyuracil, XIX., melting at 200°–210°, respectively. We also succeeded in isolating the two intermediate products of the hydrolysis, *viz.*, 1-benzyl-5-ethoxyuracil, XIV., melting at 150°, and 3-benzyl-5-ethoxyuracil, XVI., melting at 163°–164°.

[1] Behrend and Roosen: Ann. Chem. (Liebig), **251**, 240.
[2] Behrend and Roosen: *Loc. cit.*
[3] Johnson and McCollum: J. Biol. Chem., **1**, 437; THIS JOURNAL, **36**, 154.
[4] Johnson and Clapp: *Loc. cit.*
[5] *Loc. cit.*

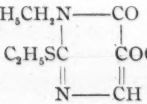
The structures of these pyrimidines were established in the following manner: The 1-benzyl-5-hydroxyuracil, XVII., melting at 230°, and the corresponding ethyl ether, XIV., reacted with diazobenzenesulphonic acid in presence of sodium hydroxide, giving beautiful red colors. The isomeric benzyl hydroxyuracil, XIX., melting at 200°–210°, and its ethyl ether, XVI., did not react with the sulphonic acid, with formation of red colors, indicating that these pyrimidines are 3-benzyl derivatives, as represented by the formulas above.

The benzyl-5-hydroxyuracils and their ethyl ethers are difficultly soluble in water. The hydroxyuracils are weak acids and stable in the presence of hydrochloric acid below 100°. 1-Benzyl-5-hydroxyuracil, XVII., was converted practically quantitatively into 5-hydroxyuracil (isobarbituric acid), XV., when heated with concentrated hydrochloric acid at 150°–160°.

1-Benzyl-5-hydroxyuracil, XVII., was converted quantitatively into 1-benzylisodialuric acid, XVIII., when it was suspended in cold water and then dissolved by adding a molecular proportion of bromine. The isodialuric acid crystallized from hot water without decomposition and gave a violet colored salt with barium hydroxide.

EXPERIMENTAL PART.

1-Benzyl-2-ethylmercapto-5-ethoxy-6-oxypyrimidine,



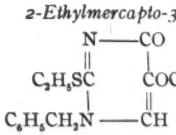
—2-Ethylmercapto-5-ethoxy-6-oxypyrimidine[1] (34 grams) and one molecular proportion of potassium hydroxide (9.0 grams) were dissolved in 250 cc. of boiling, absolute alcohol. Twenty-one and five-tenths grams of benzyl chloride were then added and the solution boiled until it gave no alkaline reaction when tested with moist turmeric (about 2 to 2.5 hours). The undissolved potassium chloride was then separated by filtration and the excess of

[1] Johnson and McCollum: *Loc. cit.*

alcohol removed by evaporation on the steam bath. We obtained a syrup which completely solidified after trituration with about 30 to 50 cc. of a 10 per cent solution of sodium hydroxide. When the alkaline solution was acidified with acetic acid we recovered 3.8 grams of the unaltered 2-ethylmercaptopyrimidine. The crude benzylpyrimidines were then extracted 3 times with boiling ether and the ether solutions saved (see 3-benzyl derivative below). The 1-benzylpyrimidine was insoluble in ether and melted without further purification at 134°–136° to an oil. It was purified for analysis by recrystallization from acetone or hot water. It separated in slender prisms melting at 140°–141° to an oil without effervescence. The compound is very soluble in alcohol, benzene, and acetone. It crystallizes from water in anhydrous condition. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{14}ON_2S$.	Found. I.	II.
N	9.65	9.81	9.80

2-Ethylmercapto-3-benzyl-5-ethoxy-6-oxypyrimidine,



C_2H_5SC COC_2H_5.—When the ether washings from the $C_6H_5CH_2N$ —— CH

above experiment were heated on the steam bath to remove the ether we obtained a syrup which partially solidified after standing for 3 to 4 days. The crystalline material was separated from a small amount of oil by suction filtration and recrystallized from 95 per cent alcohol. It deposited, on cooling, in heavy, prismatic crystals which melted at 85°–86° to a clear oil with no effervescence. The pyrimidine is very soluble in acetone, alcohol, and ether, but insoluble in cold water. Analysis (Kjeldahl):

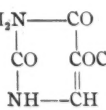
	Calculated for $C_{15}H_{18}O_2N_2S$.	Found.
N	9.65	9.30

The total yields, and relative proportions of the crude isomeric benzylpyrimidines obtained in 4 experiments by alkyla-

tion of the mercaptopyrimidine, are given in the following table:

	Weight of 2-ethylmercaptopyrimidine taken. Grams.	Weight of crude 1-benzyl derivative obtained. Grams.	Weight of crude 3-benzyl derivative obtained. Grams.	Weight of unaltered 2-ethylmercaptopyrimidine recovered. Grams.	Percentage yield of 1- and 3-benzyl derivatives.
1	47·5	36·0 or 59·3%	24·7 or 40·7%	2·5	93·4
2	34·0	23·5 or 57·3%	17·5 or 42·7%	3·8	94·0
3	18·0	16·0 or 80·0%	4·0 or 20·0%	3·0	92·5
4	5·0	4·5	..	..	..

1-Benzyl-5-ethoxyuracil,



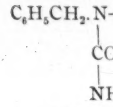
—This pyrimidine was always obtained mixed with 1-benzyl-5-hydroxyuracil (see below) by hydrolysis of 1-benzyl-2-ethylmercapto-5-ethoxy-6-oxypyrimidine with concentrated hydrochloric acid. In one experiment, 5 grams of the mercaptopyrimidine were dissolved in 150 cc. of concentrated hydrochloric acid and the solution boiled for 12 hours. When the hydrochloric acid was removed, by heating on the steam bath, we obtained a mixture of the ethoxypyrimidine and benzylhydroxyuracil melting at 140°–180°. They were separated from each other by fractional crystallization from 95 per cent alcohol. This pyrimidine was more soluble in alcohol than the hydroxyuracil and crystallized in characteristic hexagonal prisms melting at 150° to an oil. This melting point was not raised by recrystallization from water. The pyrimidine did not contain water of crystallization and did not give a test for sulphur. When

it was dissolved in bromine water, and barium hydroxide added to the solution, a purple precipitate was obtained.

The pyrimidine reacted with diazobenzenesulphonic acid, in presence of sodium hydroxide, giving a brilliant, red colored[1] solution. The color slowly faded on standing. Analysis: 0.1160 gram of substance gave 11.8 cc. N at 19° and 759 mm.

	Calculated for $C_{13}H_{14}O_3N_2$.	Found.
N	11.38	11.6

1-Benzyl-5-hydroxyuracil (*1-Benzylisobarbituric Acid*),



$C_6H_5CH_2.N{-}{-}CO$ / CO $C.OH$ / $NH{-}{-}CH$

—2-Ethylmercapto-1-benzyl-5-ethoxy-6-oxypyrimidine is not converted quantitatively into this pyrimidine by boiling with hydrochloric acid. In order to obtain a complete hydrolysis within a few hours we found it necessary to proceed under the following conditions: 36 grams of the mercaptopyrimidine were dissolved in about 500 cc. of concentrated hydrochloric acid and the solution evaporated to dryness. We obtained a crystalline mixture of the intermediate ethoxypyrimidine (see above) and the benzylhydroxyuracil, which was then dissolved in 40 to 50 cc. of hydrobromic acid. After 3 to 4 hours' digestion with this acid the hydrolysis was complete. Too long digestion with hydrobromic acid is not advisable because the benzylhydroxyuracil slowly undergoes decomposition with formation of benzyl bromide and 5-hydroxyuracil. After removal of the hydrobromic acid the pyrimidine was purified by several recrystallizations from alcohol and water. The yield was good. The pyrimidine is less soluble in alcohol than the corresponding ethoxy derivative (see above). It crystallizes from alcohol in clusters of radiating prisms melting at 230° to an oil with effervescence. The pyrimidine separates from hot water in corpuscular crystals resembling in appearance the crystalline form of 5-hydroxyuracil (Analysis III.). A violet purple precipitate was obtained when the

[1] Johnson and Clapp: *Loc. cit.*

pyrimidine was dissolved in bromine water and barium hydroxide added to the solution. The pyrimidine reacts with diazobenzenesulphonic acid, in presence of sodium hydroxide, giving as intense a red color as 1-benzyl-5-ethoxyuracil. Analyses:

I. 0.0925 gram substance gave 10.2 cc. N at 19° and 756 mm.

II. and III. Nitrogen by Kjeldahl method.

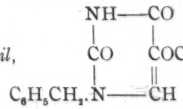
	Calculated for $C_{11}H_{10}O_3N_2$.	Found. I.	II.	III.
N	12.84	12.60	12.95	13.0

5-Hydroxyuracil (Isobarbituric Acid) from 1-Benzyl-2-ethylmercapto-5-ethoxy-6-oxypyrimidine.—About 3.5 grams of the mercaptopyrimidine were dissolved in 50 cc. of concentrated hydrochloric acid and the solution heated for 3 hours at 150°–160°. When the tube was opened there was no pressure, and oil floated on the surface of the solution. This was separated and identified as a mixture of ethyl mercaptan and benzylchloride. When the acid solution was evaporated to dryness, we obtained a colorless substance which was difficultly soluble in water. It crystallized from hot water in hard, corpuscular crystals, which decomposed without melting at about 300°. It did not contain sulphur and chlorine. When the compound was dissolved in bromine water and barium hydroxide added to the solution, a purple precipitate was obtained. A nitrogen determination agreed with the calculated value for 5-hydroxyuracil.[1]

0.1321 gram substance gave 25.4 cc. N at 22° and 750 mm.

	Calculated for $C_4H_4O_3N_2$.	Found.
N	21.87	21.48

3-Benzyl-5-ethoxyuracil,



—This pyrimidine was formed smoothly when 2-ethylmercapto-3-benzyl-5-ethoxy-6-oxypyrimidine was digested with con-

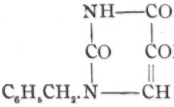
[1] Behrend and Roosen: *Loc. cit.*

centrated hydrochloric acid. It appeared to be more stable, in presence of hydrochloric acid, than the isomeric 1-benzylpyrimidine. The compound is difficultly soluble in cold water but separates from a hot solution in needlelike prisms. It is very soluble in alcohol and separates from this solvent in the form of plates. It melts at 163°–164° to a clear oil. When the pyrimidine is dissolved in bromine water and barium hydroxide is added to the solution a violet precipitate is obtained. The pyrimidine did not react with diazobenzenesulphonic acid to give a red colored solution. The solution assumed a yellow color which was permanent for 20 minutes.

Analysis (Kjeldahl):

	Calculated for $C_{13}H_{14}O_3N_2$.	Found. I.	Found. II.
N	11.38	11.23	11.40

3-Benzyl-5-hydroxyuracil (*3-Benzylisobarbituric Acid*),

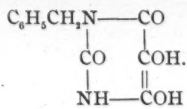


.—This compound was obtained when 2-ethylmercapto-3-benzyl-5-ethoxy-6-oxypyrimidine was digested for several hours with hydrobromic acid. The pyrimidine crystallized from acetic acid in irregular crystals which melted from 200° to 210° according to the rate of heating. It was difficultly soluble in water and alcohol.

Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}O_3N_2$.	Found.
N	12.84	12.63

1-Benzylisodialuric Acid,



.—Five and eight-tenths grams of finely pulverized 1-benzyl-5-hydroxyuracil were suspended in 50 cc. of ice water, and 4.5 grams of bromine slowly added to the solution with constant stirring. The bromine immediately disappeared and the pyrimidine

completely dissolved. The excess of water was then removed by distillation under diminished pressure at a temperature of 50° to 70°. The isodialuric acid finally separated from the warm, saturated solution in beautiful, prismatic crystals. The solution was then cooled and the crystals separated by filtration. The yield of crude material was 6.1 grams. The pyrimidine is very soluble in hot water and separates, on cooling, in lenticular crystals melting at 139° with effervescence. The pyrimidine dissolved in a solution of barium hydroxide with formation of a violet colored solution. When heated at 105° the pyrimidine slowly underwent decomposition.

Analysis:

0.0979 gram substance gave 10 cc. of N at 20° and 768 mm.

	Calculated for $C_{11}H_{10}O_4N_2$.	Found.
N	11.96	11.81

NEW HAVEN, CONN.,
June, 1908.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXIV.—RESEARCHES ON PYRIMIDINES: THE THIO DERIVATIVES OF URACIL AND THE PREPARATION OF URACIL IN QUANTITY.

[FORTIETH PAPER.]

BY HENRY L. WHEELER AND LEONARD M. LIDDLE.

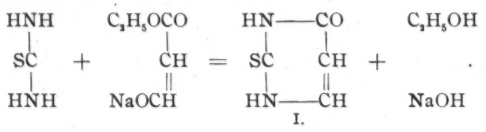
The impression is given in several text-books that the preparation of uracil, thymine, and cytosine by our synthetic methods[1] is no easier than the isolation of these substances from nucleic acids. Our syntheses are even given in Beilstein[2] as a process of formation (*Bildung*) and not as the best method of preparation (*Darstellung*). This view of our work is far from correct. In the past few years we have prepared a number of kilograms of these pyrimidines by our methods. The preparation of this amount of these substances from the nucleic acids would be a task for a factory.

[1] Wheeler, Merriam, and Johnson: THIS JOURNAL, **29**, 478 and 492 (1903).
[2] Ergänzungsbände, IV., 550, 551, 1162.

For the preparation of uracil the sodium salt of formyl-acetic ester, $NaOCH=CHCO_2C_2H_5$,[1] was condensed, in alkaline, aqueous solution, with a pseudothiourea, $H_2N—C(SC_2H_5)NH$. The condensation product, 2-ethylmercapto-6-oxypyrimidine, on boiling with hydrochloric acid, easily gave off mercaptan, and a quantitative yield of uracil was obtained.

In this paper we describe a method of preparing uracil that is an improvement even over our previous synthesis. It has been our experience that thiourea gives uniformly larger yields of pyrimidine derivative than ethylpseudothiourea[2] when condensed with the sodium salt of formyl acetic ester.

The condensation with thiourea takes place with the formation of 2-thiouracil, I.,[3] as follows:



I.

This condensation has the advantage over our previous method of avoiding the presence of mercaptan and since 2-thiouracil is more than ten times less soluble than 2-ethyl-mercapto-6-oxypyrimidine it separates more nearly completely on acidifying.

It remained then to discover a simple method of replacing the sulphur in this substance by oxygen. 2-Thiouracil, like other compounds of this class, is not desulphurized readily, if at all, by the ordinary methods. It forms more or less stable salts with the metallic oxides. List had a similar ex-

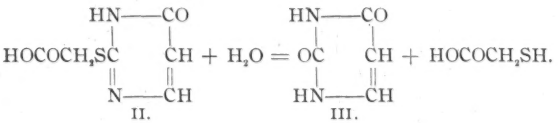
[1] Wislicenus: Ber. d. chem. Ges., **20**, 2931 (1887).

[2] We have repeated our earlier attempts to condense the sodium salt of ethyl formylacetate with urea in aqueous solution, and thus obtain uracil directly, but without success. We have found that pyrimidine condensations which fail when water is used as the solvent may be brought about in alcoholic solution, in the presence of sodium ethylate. When the sodium salt of ethyl formylacetate, urea, and sodium ethylate were warmed for an hour on the steam bath and then tested for uracil with bromine water and barium hydroxide (J. Biol. Chem., **3**, 183 (1907)) no color was obtained. No precipitate was formed on acidifying the concentrated solution and no evidence of the formation of uracil was observed.

[3] Wheeler and Bristol: THIS JOURNAL, **33**, 458 (1905).

perience with 2-thio-4-methyluracil.[1] To desulphurize this substance it was necessary to heat in a closed tube with hydrochloric acid for a few hours at 150°–160°. The thiohydantoins evidently also belong to this class.[2]

After a number of experiments we found that when 2-thiouracil was simply boiled with an aqueous solution of chloracetic acid, in slight excess, sulphur was easily removed, and on evaporation uracil remained. The yield was practically quantitative. The reaction probably involves the intermediate formation of the unstable 6-oxypyrimidine-2-thioglycollic acid, II., which, as we show below, on boiling with water gives uracil, III., and thioglycollic acid or its decomposition products, as follows:



II. III.

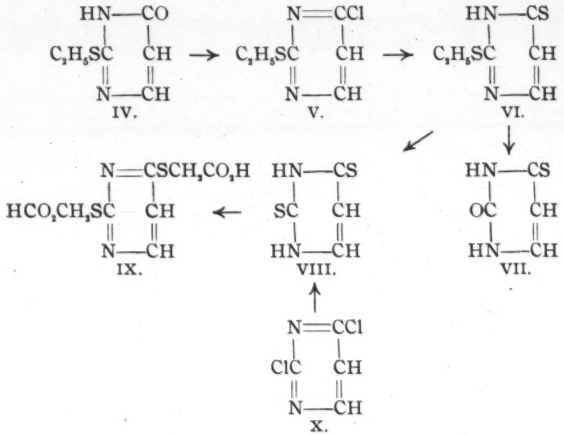
This reaction, which introduces nothing which can not be easily removed, is so smooth and satisfactory that we intend to investigate the use of chloracetic acid for desulphurization in other cases. At present, we have examined simply the new thio derivatives of uracil in this respect and have made the curious observation that while 2-thiouracil and 6-thiouracil, VII., are readily desulphurized, 2,6-dithiouracil, VIII., is not desulphurized on boiling with chloracetic acid but apparently forms the stable pyrimidine, 2,6-dithioglycollic acid, IX.

The preparation of the new thio derivatives of uracil was carried out as follows: 2-Ethylmercapto-6-chlorpyrimidine, V., from 2-ethylmercapto-6-oxypyrimidine,[3] IV., was treated with potassium hydrosulphide, giving 2-ethylmercapto-6-thiopyrimidine, VI.

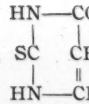
When this compound was treated with concentrated hydrochloric acid on the steam bath mercaptan was evolved and

[1] Ann. Chem. (Liebig), **238**, 1 (1886).
[2] Bailey and Randolph: Ber. d. chem. Ges., **41**, 2495 (1908).
[3] Wheeler and Johnson: THIS JOURNAL, **29**, 496 (1903).

6-thiouracil, VII., was formed. On heating with dry hydrogen chloride, ethyl chloride was given off and 2,6-dithiouracil, VIII., was obtained. The latter was also prepared from 2,6-dichlorpyrimidine, X., and potassium hydrosulphide.



EXPERIMENTAL PART.

2-Thiouracil,  .—The sodium salt of formylacetic ester, prepared according to Wislicenus'[1] directions from 150 grams of ethyl formate, 150 grams of ethyl acetate, and 42 grams of sodium clippings in 500–600 cc. of dry ether, was dissolved in a cold, saturated, aqueous solution of 70 grams of thiourea. The solution was allowed to stand for an hour or so, then warmed on the steam bath, and finally cooled and acidified with acetic acid. Four such experiments gave about 280 grams of 2-thiouracil.

[1] Ber. d. chem. Ges., **20**, 2933 (1887).

A portion of this material was crystallized from water until it was obtained in colorless bunches of prismatic plates which melted with decomposition at about 340°. A solubility determination was then made as follows: The substance was placed in cold water and a rapid stream of air was drawn by suction, first through a wash bottle containing distilled water, and then through the solution containing the suspended substance. After two hours the undissolved material was filtered off and a weighed portion of the solution was evaporated to dryness and the residue was heated to constant weight at 110°.

To check the results a parallel series of determinations were made in which the substance was dissolved in hot water and the saturated solution was allowed to cool while air was drawn through for two hours as before. Solubility determinations were also made in this manner in the case of 2-ethylmercapto-6-oxypyrimidine and 2-methylmercapto-6-oxypyrimidine. It was found that 100 parts of water at 17° dissolved:

	Hot saturated solution.	Cold saturated solution.
2-Thiouracil	0.0533 gram	0.0598 gram
2-Methylmercapto-6-oxypyrimidine	0.6170 "	0.6620 "
2-Ethylmercapto-6-oxypyrimidine	0.8000 "	0.7930 "

The mercaptopyrimidines are therefore more than ten times as soluble in water as 2-thiouracil. 2-Thiouracil is almost insoluble in alcohol while the mercapto derivatives are very soluble. In our pyrimidine condensations alcohol is always present as a by-product, unless removed by evaporation; this reduces the yield in the case of the mercapto derivatives while in the case of thio derivatives just the opposite is true.

In accordance with its thioamide character, 2-thiouracil is a much stronger acid than uracil. It readily dissolves in sodium or potassium hydroxides and it forms very soluble, crystalline, anhydrous salts with these bases. It can be very conveniently crystallized from aqueous ammonia in which it is far more soluble than in water. It forms an ammonium salt which loses ammonia on drying or on boiling with water. Mercuric oxide removes 2-thiouracil from solution, forming an amorphous, anhydrous, insoluble salt.

The Copper Salt, $C_4H_2ON_2SCu.H_2O$.—Copper sulphate produces in aqueous solutions of 2-thiouracil, with or without alkali, an amorphous, mustard-yellow, insoluble precipitate. This salt can be boiled with water without alteration. It was dried in a desiccator over calcium chloride for analysis.

0.2997 gram substance lost 0.0276 gram on heating two hours at 105°–115°.

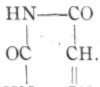
	Calculated for $C_4H_2ON_2SCu.H_2O$.	Found.
H_2O	8.67	9.20

0.1167 gram substance gave 0.045 gram CuO.

	Calculated for $C_4H_2ON_2SCu.H_2O$.	Found.
Cu	30.60	30.76

When silver nitrate is added to an aqueous solution of 2-thiouracil an amorphous, gelatinous, white precipitate is formed which does not blacken on boiling.

Preparation of Uracil,



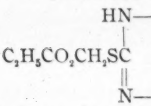
—Twenty grams of 2-thiouracil were boiled with one and a half molecular proportions of chloracetic acid in a large amount of water for one hour, then evaporated to dryness on the steam bath. The slightly colored residue was decolorized by means of animal charcoal, and on concentrating the solution 14.2 grams of pure white uracil, free from sulphur, were obtained. The yield in this case was 81 per cent of the calculated. More could have been obtained from the mother liquor.

In another experiment 30 grams of 2-thiouracil were boiled with 33 grams of chloracetic acid in about 700 cc. of water. When the material had dissolved the solution was allowed to evaporate to dryness on the steam bath. The residue was warmed with alcohol, filtered, and washed with alcohol. It was then free from sulphur and weighed 23.5 grams. This is 89.5 per cent of the calculated.

Uracil from 6-Thiouracil.—An aqueous solution of 2.1 grams of 6-thiouracil was mixed with 3 grams of chloracetic acid and

the solution was then evaporated to dryness on the steam bath. When the residue was crystallized from water 1.2 grams of pure uracil separated. This is 66 per cent of the calculated.

Ethyl 6-Oxypyrimidine-2-thioglycollate,

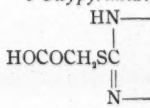


$C_2H_5CO_2CH_2SC_4H_2N_2O.\frac{1}{2}H_2O$.—Five grams of 2-thiouracil were mixed with a solution of 0.9 gram of sodium in 30 cc. of alcohol and then 4.8 grams of ethyl chloracetate were added. The mixture was heated on the steam bath under a return condenser for one hour. The solution was then filtered and allowed to evaporate under reduced pressure in a desiccator. The crystalline residue after three recrystallizations from water yielded long, thin, glistening plates. These gave a strong test for sulphur and melted to a clear oil at 154°–155°. The substance was easily soluble in hot water and hot alcohol and nearly insoluble in cold water.

0.2852 gram substance lost 0.0138 gram when heated at 100°–115° for two hours.

	Calculated for $C_8H_{10}O_3N_2S.\frac{1}{2}H_2O$.	I.	Found. II.	III.
H_2O	4.03	....	....	4.83
N	12.55	12.44	12.57	....

6-Oxypyrimidine-2-thioglycollic Acid,



$HOCOCH_2SC_4H_2N_2O.H_2O$.—This acid was obtained from the above ester by warming its aqueous solution with an excess of potassium hydroxide for a few minutes on the steam bath. The solution was then cooled and acidified with hydrochloric acid. A heavy, white precipitate formed which crystallized from water in bunches of fine prisms. This proved to be the hydrous form which separates slowly and melts at 178°. If the solution is stirred or the beaker scratched the anhydrous form generally results. The latter separates rapidly in loose

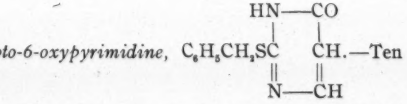
bunches of fine needles. The substance can be crystallized from alcohol. When it is boiled with water, thioglycollic acid separates and uracil is obtained.

0.2676 gram substance lost 0.0238 gram when heated two hours at 105°–110°.

	Calculated for $C_6H_6O_2N_2S.H_2O$.	Found. I.	II.	III.
H_2O	8.82	8.89	....	....
N	13.72	....	13.90	13.65

Some experiments were made with the object of preparing alkyl derivatives of 2-thiouracil. If a smooth alkylation on the sulphur would take place it would be the best method for the preparation of 2-alkylmercaptopyrimidines.

2-Ethylmercapto-6-oxypyrimidine.[1]—The action of sodium ethylate and ethyl iodide on 2-thiouracil in alcoholic solution gave 2-ethylmercapto-6-oxypyrimidine, melting at 152°. When 30 grams or more of 2-thiouracil were employed the yields were much below the calculated. Unaltered 2-thiouracil was recovered when the substances were allowed to act in molecular proportions. It required repeated recrystallizations from alcohol to remove this impurity, so that the yields were unsatisfactory. If an excess of iodide and alkali were used the yield of 2-ethylmercapto-6-oxypyrimidine was still further reduced, owing to the formation of higher alkylated products. It was found that benzyl chloride acted more smoothly.

2-Benzylmercapto-6-oxypyrimidine,  —Ten grams of 2-thiouracil and 4.4 grams of potassium hydroxide were dissolved in the smallest possible quantity of water on the steam bath and mixed with 9.9 grams of benzyl chloride. Alcohol was then added until the oil went into solution. The reaction took place immediately and gave long, slender, colorless prisms weighing 11.7 grams, or 68 per cent of the calculated.

[1] Wheeler and Merriam: THIS JOURNAL, **29**, 478 (1903).

The same quantities of substances shaken repeatedly in a separatory funnel in aqueous solution without alcohol gave 12.4 grams, or 72 per cent of the calculated. The first method of preparation is smoother and is much easier, the product being more nearly pure.

The substance is soluble in about 16 parts of hot alcohol and in 50 parts of cold. In water or ether it is practically insoluble. Recrystallization from alcohol gave slender, twinned prisms which melted to a clear oil at 192°–193°.

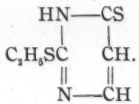
	Calculated for $C_{11}H_{10}ON_2S$.	Found.
N	12.88	12.88

When the substance was warmed with hydrochloric acid on the steam bath, benzyl mercaptan separated. On evaporating and extracting with alcohol, uracil was obtained.

The Sodium Salt of 2-Benzylmercapto-6-oxypyrimidine, $C_{11}H_9ON_2SNa.3H_2O$.—The mercapto derivative was dissolved in an aqueous solution of sodium hydroxide and allowed to crystallize slowly in a desiccator. Large talclike plates formed which were very soluble in water and fairly soluble in alcohol.

0.3069 gram of substance lost 0.056 gram when heated at 100°–110° for two hours.

	Calculated for $C_{11}H_9ON_2SNa.3H_2O$.	Found. I.	II.	III.
H_2O	18.35	18.24	....	....
N	9.52	....	9.69	9.43

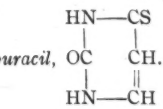
2-Ethylmercapto-6-thiopyrimidine,  —Eight grams of 2-ethylmercapto-6-chlorpyrimidine[1] were treated with two and a half times the calculated quantity of potassium hydrosulphide in alcoholic solution. The solution was boiled for about 15 minutes and then evaporated to dryness on the steam bath and the residue taken up in a small quantity of

[1] Wheeler and Johnson: THIS JOURNAL, **29**, 496 (1903); **31**, 596 (1904).

water. The solution was shaken with ether, to remove any 6-ethoxy or unaltered chlor compound, and then made distinctly acid in the cold with acetic acid. A white flocculent precipitate separated, weighing 6.4 grams, or 80 per cent of the calculated. The substance was recrystallized twice from water, when it gave brilliant needlelike prisms, having a pale yellow color, which melted to a yellow oil at 149°. The material was easily soluble in alcohol and moderately in hot water. In cold water it was nearly insoluble. The properties of the compound were very similar to those of 2-ethylmercapto-6-oxypyrimidine, but a mixture of these substances melted at about 126°.

	Calculated for $C_6H_8N_2S_2$.	Found.
N	16.27	16.05

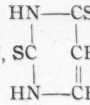
6-Thiouracil,



.—Two grams of 2-ethylmercapto-6-thiopyrimidine were evaporated to dryness on the steam bath with 10 cc. of concentrated hydrochloric acid. Mercaptan escaped. The residue was extracted with cold alcohol to remove unaltered ethylmercaptothiopyrimidine and the insoluble material was then found to weigh 0.8 gram, or 55 per cent of the calculated. In another experiment more prolonged action of acid gave a yield of 90.0 per cent; a small amount of uracil was also formed.

Like uracil and 2-thiouracil, 6-thiouracil is practically insoluble in strong alcohol but moderately soluble in hot water. It crystallized from hot water in small, light yellow needles. On rapidly heating it blackened above 270° and melted with effervescence at 328°. The properties of this substance are closely similar to those of 2,6-dithiouracil but a mixture of these compounds melted at 295°.

	Calculated for $C_4H_4ON_2S$.	Found.
N	21.87	21.66

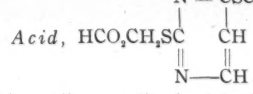
2,6-Dithiouracil,  . —A portion of 2,6-dichlorpyrimidine[1] was warmed on the steam bath with an aqueous solution containing somewhat more than four times the calculated quantity of potassium hydrosulphide. As soon as the oil disappeared, the hot solution was filtered from slight impurities and acidified with hydrochloric acid. This gave a yellow flocculent precipitate which was recrystallized from water. It was found to be difficultly soluble and it gave a feltlike mass of fine, bright yellow needles, which turned dark and decomposed above 230° without showing a definite melting point.

0.3215 gram substance gave 1.0278 gram $BaSO_4$.

	Calculated for $C_4H_4N_2S_2$.	Found. I.	Found. II.
S	44.44	43.79	....
N	19.44	....	19.46

2,6-Dithiouracil was also obtained when 2-ethylmercapto-6-thiopyrimidine was melted in an oil bath at 170° and treated with dry hydrogen chloride. The material quickly solidified in the hot bath. It was then removed and crystallized from water, whereupon the characteristic yellow needles of 2,6-dithiouracil were obtained.

It was also found that when 2-ethylmercapto-6-oxypyrimidine was treated in the same manner 2-thiouracil was formed.[2]

Action of Chloracetic Acid on 2,6-Dithiouracil: *Pyrimidine-2,6-dithioglycollic Acid*,  . —Two grams of 2,6-dithiouracil were dissolved in hot water and 5 grams of chloracetic acid were added. The solution was evaporated to dryness, the residue taken up in water and

[1] J. Biol. Chem., **3**, 287 (1907).

[2] See also Wheeler and Liddle: J. Am. Chem. Soc., **30**, 1157 (1908).

evaporated again, the operation being repeated several times or until the yellow color disappeared. The residue was then moderately soluble in alcohol and very difficultly soluble in hot water. It was crystallized from 600 cc. of boiling water, and 2 grams of white powder separated. Boiling with water or even warming with concentrated hydrochloric acid did not desulphurize this substance. When heated it decomposed above 200°.

	Calculated for $C_8H_8O_4N_2S_2$.	Found.
N	10.77	11.14

NEW HAVEN, CONN.,
September, 1908.

THE LIMITING CONDUCTIVITY AND DEGREE OF IONIZATION OF ALCOHOLIC SOLUTIONS.

BY B. B. TURNER.

The degree of ionization of alcoholic solutions cannot be determined with either the ease or the accuracy possible in the case of aqueous solutions, and in spite of numerous researches and the accumulation of a great quantity of data, there is still much uncertainty as to its value. The conductivity method suffers from two difficulties. Besides the doubt as to the validity of the usual assumption that the degree of ionization is given by the ratio of the molecular conductivity to the limiting value of the same function at infinite dilution, which probably does not hold with any great accuracy even for aqueous solutions at concentrations above half, or possibly one-tenth, normal, and may fail at still smaller concentrations in nonaqueous solutions, there is the great practical difficulty of determining the limit of the molecular conductivity, which is only reached at dilutions at which the actual conductivity is extremely small. The ebullioscopic method is free from these defects, but is only applicable to solutions of moderate concentration, and, owing to experimental difficulties, cannot give the same degree of accuracy as good electrical measurements.

The present investigation was undertaken at the suggestion of Prof. H. C. Jones, with the intention of relying chiefly upon the boiling point method as worked out and already applied by him to many alcoholic solutions. From such conductivity data as existed, it appeared probable that the molecular conductivity of solutions in ethyl alcohol would not become appreciably constant at a smaller dilution than about a million liters, and would therefore be incapable of experimental determination.[1] It has been found, however, that when necessary precautions are taken to reduce the conductivity of the solvent, and eliminate accidental fluctuations in the same during the course of each experiment, the molecular conductivity becomes appreciably constant at much more moderate dilutions. The boiling point method was tested and a great deal of time spent in various minor modifications, which, it was hoped, would increase its accuracy, but the results are not yet in a condition suitable for publication. The author hopes to be able to continue this work, and also to add to the conductivity data, but a change in circumstances makes it desirable to publish the results already obtained.

The ethyl alcohol used in this investigation was dried in the usual way by boiling with quicklime, in some cases after long standing over the same, for two or three days, and the degree of dehydration was in all cases controlled by determination of the specific gravity. As appeared in the course of the work, the conductivity alone is not a certain indication of freedom from water, as an alcohol was obtained with nearly 1 percent of water and a conductivity of only 0.183×10^{-6}

[1] The author has just become aware of a paper by Dutoit and Rappeport (J. Chim. Phys., **6**, 545, Sept., 1908) in which the limiting conductivities of several salts in ethyl alcohol are determined by measurements at 18° at dilutions up to 4000-20000 liters. Needless to say he did not know of these measurements when the work described below was being carried out (Feb.-June, 1908). In the case of potassium iodide, Dutoit and Rappeport's results agree fairly closely with the present author's, as is shown by the following table in which the values are recalculated in reciprocal ohms, but the maximum of the molecular conductivity in the neighborhood of 20000 liters is not indicated.

V.	D. & R.	B. B. T.
500	36.4	36.9
1000	38.4	39.1
2000	39.6	41.0
4000	40.7	42.0
∞	41.9	42.85

mhos, which is 5 to 10 times lower than that of the "pure" alcohol used in many previous investigations; on the other hand, the most nearly absolute alcohol used usually had a higher conductivity than this until it had been redistilled several times from a clean flask through a tin-worm condenser. The best alcohol used was about 99.98 per cent and the average of that used for the accepted results about 99.9 per cent. It may not be amiss to recall here that Mendeléeff's tables of specific gravity in Landolt and Börnstein's "Tabellen," which are widely used for the calculation of the strength of aqueous alcohols, require a slight correction when the temperature of the determination has been read on a thermometer calibrated on the hydrogen scale, as the latter scale, which the certificates of the Phys. Tech. Reichsanstalt have made familiar, was not used by Mendeléeff. While the exact magnitude of this correction cannot be determined now, it is safe to assume that it amounts to about 0.15° C., corresponding to 0.03–0.04 per cent alcohol, which must be subtracted from the values for the percentage compositions given in the tables.[1]

The conductivity of the alcohol is naturally a question of great importance where high dilutions are to be made. Fortunately there is no difficulty in reducing this about 10 times below that of ordinary "conductivity" water, and exposure to air seems to affect it much less than it does water; probably because carbon dioxide forms no compound in alcohol as readily ionized as carbonic acid is in water. Alcohol having a conductivity as low as 0.3×10^{-6} mhos can be easily obtained, and in all but the preliminary experiments the conductivity of the alcohol used was below 0.2×10^{-6}, the average being about 0.15×10^{-6}, while in some cases it was as low as 0.080 to 0.075×10^{-6}.[2] To reduce exposure to the air as much as possible, the alcohol was at first stored in a bottle with a syphon of Jena glass, through which it was forced as needed by a rubber blowing-ball, but this precaution was found to be dispensible.

[1] See Andrews: J. Am. Chem. Soc., **30**, 359 (1908).

[2] These results agree almost exactly with those of Völlmer (Wied. Ann., **52**, 328 (1894)). The use of alcohol with considerably greater conductivity, approaching that of distilled water, seems hardly permissible.

The most important detail of practical manipulation proved to be the manner of making up solutions. To avoid frequent additions of solvent and withdrawals of solution, which give opportunity for absorption of water, as well as for accidental contamination with other electrolytes, and in order to insure greater accuracy in the dilutions, it was decided not to follow the Ostwald method of dilution in the cell, but to make up all solutions on a considerable scale in measuring flasks, from which the cell was filled after repeated rinsings. To insure accuracy, the cell was always refilled once more after making a measurement and the observation repeated; if the two differed appreciably, a third was taken. The necessity for this was found to depend on the past history of the cell.

Platinum electrodes in alcoholic solutions of salts seem to show a certain amount of absorption, such as has been described by Kohlrausch in the case of aqueous solutions of acids and bases, but not of salts. After a cell had been used for solutions of medium strength and thoroughly rinsed with a very dilute solution, a further slight decrease in conductivity was observable on refilling with the same, and sometimes constancy is not reached till the third or fourth observation. Allowing the solution to stand for 20 minutes to an hour in the cell before reading proved helpful, as though equilibrium were only attained by slow diffusion of the electrolyte out of the electrodes. A contrary but less noticeable tendency of the conductivity to increase when stronger solutions were used after weak ones was sometimes observed; evidently the residual diffusion of salt into the electrode was less in proportion to the total conductivity. I therefore made a habit of commencing a series of observations with the pure solvent, followed by the solutions in increasing order of strength. Platinized electrodes were naturally worse in this respect than bright ones, so that the latter were used wherever possible, and always in the best determinations at high dilutions and with the pure solvent.

The cells used were mostly of the well-known Arrhenius form as modified by Jones and Bingham,[1] with fixed electrodes fused into ground-glass stoppers. While this

[1] THIS JOURNAL, **34**, 493 (1905).

form has advantages in cleanliness and ease of manipulation, there is some danger of variation in the cell constant, due to the scraping of the electrodes against the sides of the cell in taking them out. With care in manipulation the error from this source is not appreciable when the distance between the plates is several millimeters, but as the influence of any slight distortion increases in inverse proportion to the distance between the plates, it is not advisable to make this less than about a millimeter. Even where the distance was about 5 mm. a change of nearly one-half per cent occurred during the course of the work, and was only detected on recalibration considerably later. In order to get a sufficiently high constant for the very pure solvent and for dilutions of 100,000 liters and over, I made a cell consisting of two platinum plates, 5 x 5 cm., rolled and welded in the form of cylinders, which were fixed concentrically by wires fused into tubes of Jena glass, and kept at a constant distance apart of about 1 mm. by means of drops of fusible glass. The glass tubes, which served as mercury cups to make electrical connection, were fastened in a cork which nearly closed the mouth of a Jena glass tube about 2 cm. in diameter and closed at the bottom. The constant of this cell being only 5.5, the resistance with the purest alcohol was about 35,000 to 70,000 ohms, which was low enough to be measured with sufficient accuracy. A great advantage in this form of cell is that the electrodes slide in and out smoothly, and having considerable stiffness owing to their cylindrical shape, any accidental contact with the sides of the cell has very little tendency to distort them. Stirring of the solution was effected by lifting and lowering the electrodes several times.

One very vital question in accurate work with alcoholic solutions has to do with the possible oxidation of the alcohol to acetic acid, during the experiments, by exposure to the air. That this did not play any serious part in this work is shown by the following experiment:

Three cells, with platinized electrodes, which had been allowed to stand a couple of days after using, the electrodes

remaining wetted with pure alcohol, were rinsed out with the same small quantity (about 42 grams) of a very pure alcohol whose conductivity had just been found to be 0.10×10^{-6} mhos and the rinsings were then returned to the measuring cell. The conductivity was now 0.37×10^{-6}, showing an increase of only 0.27×10^{-6} due to the whole amount of acetic acid washed out of the three cells. As the conditions for oxidation were so much more favorable than in the usual course of the measurements, when the electrodes were totally covered by the alcohol, and as the time was so much longer, it is reasonable to suppose that the gain in conductivity of a sample of alcohol during an experiment could hardly exceed one or two hundredths of a reciprocal megohm, and was probably less. The bright platinum of the cell used for the high dilutions would be much less likely to cause oxidation. If oxidation did occur in the course of the experiments it would show itself in a gain in conductivity on lifting out the electrodes to stir the liquid, and still more on allowing the cell to stand between two measurements. No evidence of a definite change could be noticed in the first case, but only the slight accidental changes due to differences in position of the electrodes, which it was the special object of these repetitions to test. Change on standing was more noticeable, but instead of a gain there was an almost uniform *loss* of conductivity, especially marked with the purest alcohols and most dilute solutions, if the alcohol had been recently distilled. A similar change in the conductivity of alcohol has been observed by Pfeiffer,[1] who attributes it to the solution of oxygen from the air. While there is nothing in my observations to exclude this view, it is difficult to see why a solution of oxygen in alcohol should act as an anti-electrolyte, or, in other words, why the oxygen should decrease either the number or the migration velocity of whatever ions may be present in pure alcohol. It seems to me more likely that the observed decrease in conductivity is the result of a chemical change, which may or may not be connected with the taking up of oxygen from the air,

[1] Pfeiffer: Wied. Ann., **38**, 31 and 226 (1885).

removing some trace of electrolytic impurity, perhaps an ethyl peroxide, in the fresh alcohol. This change seems to be accelerated by platinum, but the conductivity of the alcohol was observed to decrease even in the bottle, as is shown by the following observations:

A sample of alcohol of the sp. gr. 0.78948 at 20°/4 gave a conductivity, when first tested, two or three days after distillation, of 0.126×10^{-6} reciprocal ohms, which decreased to 0.105 two days later. Another sample gave 0.126 on April 30th and 0.111 on May 1st. When allowed to stand in the cell in contact with bright platinum overnight, another alcohol decreased in conductivity from 0.224 to 0.189. The change becomes slower after a few days. Thus a sample giving 0.224 on March 24th gave 0.195 on April 16th, a loss of only 0.03 in 23 days. As against this, there was frequently a gain in conductivity on standing overnight in the cell, due to solution of minute amounts of substance either from the glass or the platinum electrodes, and this was so much increased on heating that it was impossible to obtain concordant results for the temperature coefficient of the purest alcohols, as will be shown later.

The action of absolute alcohol on glass is much less than that of water. A sample kept for 26 days in an ordinary glass bottle, protected from the air by a drying tube, increased only 0.1×10^{-6} mhos, and in Jena glass the gain was naturally less.

A much more marked effect was found in the behavior of alcohol of very low conductivity on bringing it into a new vessel which had been thoroughly cleaned and dried in the ordinary way, and in this was found the great cause of the earlier inconsistent results at high dilutions. The act of drying seems to loosen the surface of the glass, or else the solvent action is so much increased by the higher temperature that even in the short time in which the drops of water remain on the glass enough is acted on to greatly increase the conductivity of the alcohol which is afterwards put in the vessel. This source of error may be largely avoided by using only vessels which have been freed from water by *rins-*

ing with alcohol of the required purity, and never allowed to dry after washing. Thus an alcohol giving a conductivity 0.174×10^{-6}, when sampled from the stock bottle, gave 0.185, 0.181, 0.195, respectively, after pouring into three measuring flasks which had been rinsed, as above, but 0.356 and 0.410 in two others which had been equally carefully cleaned, then rinsed with ordinary distilled water, then three times with "conductivity" water of about 2×10^{-6}, and then dried by heating for a few minutes in a clean drying oven and blowing out the steam with a current of filtered air. From this experiment it was plain that discrepancies in previous work at dilutions of over 10,000 liters, at which the total conductivity is less than 5×10^{-6}, were due to an increase in the conductivity of the solvent between the time at which it was measured alone and its introduction as solution into the measuring cell. It was therefore made a uniform custom to test the conductivity of *each* quantity of alcohol used for a dilution *after* it had been poured into the measuring flask, just before making the solution; the cell itself having been thoroughly cleaned by rinsing with conductivity alcohol, assurance of which was obtained by taking its resistance in the process, there remains only the possibility that impurity may be introduced from the surface of the pipette. To test this, 10 cc. were drawn up into a clean pipette from the alcohol in the cell after its conductivity had been found to be 0.116×10^{-6}, and allowed to run back. The conductivity was then 0.122. As the pipette was used only to deliver solutions with a conductivity many times greater (usually 200 to 500×10^{-6}), this increase would be quite inappreciable. Even where the correction for the solvent amounted to a large fraction of the total conductivity, it was not thought necessary to apply any correction for such an increase, inasmuch as the much larger volume of alcohol in the measuring flask would reduce this correction to about 0.001 or 0.002. Care must be taken, however, not to use the *mouth* in pipetting, on account of the danger of introducing carbon dioxide. In all the later experiments the pipette was filled by the help of a suction pump.

Solutions up to about N/250 were made by direct weighing, and from these the higher dilutions were made by volume. In order to avoid the chance of error in repeated dilutions, flasks up to 250 cc. and a 2 cc. pipette were used when necessary, and to avoid the uncertainty as to the amount delivered, the flask, containing some alcohol, was weighed before and after running in the quantity from the pipette, from which the volume actually delivered could be ascertained to less than 0.01 cc. by means of an approximate value for the specific gravity.

All the concentrations are calculated on the basis of *volume normality* at 20°. In comparison with the results of the boiling point method it must not be forgotten that the latter are usually expressed as molecular concentrations *per gram* of alcohol, and therefore appear to be about 20 per cent higher. Conductivities are expressed in *reciprocal ohms*, not, as is still frequently done, in Siemen's units.

Measurements were made at several different temperatures and especially at as high temperatures as practicable, with the object of ascertaining the degree of ionization at the boiling point for comparison with the ebullioscopic method. It was found quite possible to make reasonably satisfactory measurements at 65° C., though many solutions were not measured above 50°. The better to obtain the change of the temperature coefficient with temperature, measurements were also made at 0° C. It was found, in fact, that while the conductivity-temperature curve for the stronger solutions is nearly a straight line, in the case of very dilute solutions it has a decided curvature, so that very incorrect results would be obtained for the limiting value of the molecular conductivity at 78° by linear extrapolation with a temperature coefficient obtained by measurements in the neighborhood of 25° C. As a check on the accuracy of the extrapolation, two solutions were finally measured at 78° in specially made cells of Jena glass which were sealed with the blowpipe and completely immersed in the bath, except for a side tube that served as a handle, in such a way as to avoid distillation of the cell contents from one part of the cell to another.

Slight indications of this trouble were sometimes noticed in the usual type of cell, but not enough to affect the results by more than one or two parts in a thousand. The bath used was jacketted with asbestos and covered with an asbestos lid, and could be kept constant to 0°.1 by an Ostwald thermo-regulator.

In working at 50° and 65° decided changes in conductivity, especially of the more dilute solutions, were noticed when the same solution was tested at 25° before and after heating. In some cases the conductivity increased, indicating concentration by evaporation or solution of impurities, but more often at high dilutions there was a decrease of conductivity, amounting sometimes to 2 per cent or more. This decrease seems to be due to a change in the conductivity of the alcohol itself, as its relative importance is roughly proportional to the dilution, the absolute amount of the change averaging about 0.1×10^{-6}. For this reason the molecular conductivity at the higher temperatures could not be calculated directly without correction. I have assumed that the change, if not complete at the higher temperature, at least comes to a standstill, within the limits of experimental error, on rapid cooling to 25°, and I have therefore compared the conductivities at 50° and 65° with that at 25° *after* heating, in calculating the temperature coefficients. From these temperature coefficients and the original conductivities at 25°, the true conductivities at the higher temperatures are calculated.

The apparent temperature coefficient for alcohol itself varies, as has been said, with the age and previous history of the sample; in fact the absorption of impurities by the alcohol from the vessel or by the platinum electrodes from the alcohol, together with the time change in conductivity, due, as supposed by Pfeiffer, to saturation with air, may entirely mask the true temperature effect. However, it was evident that while for ordinary alcohol with a conductivity down to about 0.3×10^{-6}, the temperature coefficient, like that for dilute solutions of salts, is high, for the purest alcohol obtained it was much smaller, if indeed it was not zero or even negative. Thus the conductivity of one sample of alcohol originally

0.3×10^{-6} at 25° was increased by 50 per cent when the temperature was raised to 50° C., while the conductivity of another sample rose from 0.110 at 20° to only 0.112 at 30° and gave 0.116 when again cooled to 20°; another gave sensibly the same conductivity, 0.138, at 20° and 35°. A conductivity of 0.22 at 25°, which was practically unchanged before and after heating, was reduced to 0.185 at 50°, indicating a *negative* temperature coefficient of —0.007 per degree. At 0° the conductivity was always found to be less than at 25°. A proper determination of this point, which would be of considerable interest, was outside the scope of the present investigation.

Only one substance has so far been studied with any completeness. Potassium iodide was chosen because it could be readily obtained pure (my sample gave: iodine, 76.37 and 76.44 per cent; calculated, 76.42; contained no iodate and barely perceptible traces of other halogens, and gave a clean violet flame test), and on account of the number of researches in which this substance has been included and which are available for comparison. Lithium chloride was also investigated but the figures given are subject to revision. One series of measurements was made with lithium bromide to which much weight cannot be attached as, owing to its hygroscopic character, a considerable amount of moisture was introduced with the salt.

One experimental point of some importance remains to be mentioned. Results differing by several per cent could be obtained for the resistance of the alcohols and most dilute solutions according as the connections of the telephone were made one way, or the wires interchanged. This asymmetry of the telephone, noticed by Kohlrausch, must not be neglected when working with very dilute solutions, for as its disturbing effect is not constant, the relative values for large and small resistances will not be correctly measured. As soon as discovered, the error was eliminated by taking the mean of the resistances found in the two positions, two or more readings on the bridge being taken each way. Comparison of numerous readings so obtained shows that the

proportional error increases roughly proportionately to the resistance, averaging about ±0.15 per cent for a resistance of 1000 ohms, ±1 per cent for about 7000 ohms, ±2 per cent for 15000 ohms, and so on. It should be directly determined, where appreciable, as variations from ±3 to ±7 per cent were found with alcohols giving resistances of 45,000 to 50,000 ohms. Some of the results in the earlier series have been corrected by means of these averages, the effect on the molecular conductivity found being only a small fraction of a unit.

Resistances were measured by the usual Kohlrausch method. It need hardly be mentioned that thermometers, bridge wire, weights, etc., were carefully calibrated. Molecular weights are calculated on the basis o = 16. The volumes are expressed in *true* liters. The standard temperature adopted for the making up of solutions was 20°, and where the solutions differed appreciably from this, they were corrected with the approximate expansion coefficient, 1.001 per 1° C. In Table I. are given only the results for high dilutions; the numerous results at dilutions below 1000 vary so little from a regular curve (about ±0.2 unit) that the individual observations have no particular interest. The figures in brackets are those which are obviously erroneous. Only the last three series were carried out with all the precautions described above, and all the results so obtained are given.

Table I.—Molecular Conductivities in Reciprocal Ohms of Potassium Iodide at 25° at High Dilutions.

$V \times 10^{-3}$ liters.	μ	$V \times 10^{-3}$ liters.	μ	$V \times 10^{-3}$ liters.	μ
Series I.		Series III.		Series V.	
0.98	43.8	12	48.36	2.95	47.1
24.4	48.5	149.6	[69]	8.52	48.26
179.5	[59]			51.8	46.5
				129.3	47.2
Series II.		Series IV.		Series VI.	
3.92	47.3	2.23	46.83	4.0	47.0
12.58	46.6	22.7	49.4	11.5	47.81
31.19	[51]	141.0	[43.4]	20.1	47.88
31.57	48.6	142.3	49.3	148.6	44.6
62.9	44.8	452.0	46.1	Series VII.	
157.3	[69]			10.1	49.11
				17.5	47.7

Table II.—Ratios of Molecular Conductivity of Potassium Iodide at t° to its Value at 25°.

V liters.	$t = 0°$.	18°.	50°.	65°.	78°.
12	0.673	0.904	1.335	1.5	....
13.1	0.67	...	1.39	(1.53)	1.73
16	0.67	0.90	1.34	1.55	....
32	0.672	0.90	1.36	....	....
64	0.665	0.90	1.38	1.6	(1.8)
128	0.655	0.89	1.41	....	....
250	0.64	0.89	1.44	1.63	(1.85)
500	0.64	0.889	1.47	....	....
1000	0.63	0.888	1.48	1.8	(2.1)
5000	0.63	0.885	1.486	1.8	....
10000	0.62	0.884	1.488	1.83	2.18

Table III.—Molecular Conductivities of Potassium Iodide.

V.	0°.	18°.	25°.	50°.	65°.	78°.
10	(14.8)	20.1	22.2	29.7	(34)	....
12	15.4	20.8	23.0	30.5	35.2	(40)
13.1	15.6	21.0	23.3	31	(35.8)	40.5
16	16.3	21.7	24.1	32.4	37.3	...
32	18.5	24.8	27.5	37.4	43	...
64	20.8	28.0	31.1	43.0	(50)	...
128	23.0	31.4	35.0	49.5	57	(64)
250	24.6	34.1	38.2	55	63	...
500	26.4	36.9	41.4	60.4	69	...
1000	27.9	39.1	44.0	65	75	(90)
5000	30.0	42.3	47.8	71	87	...
10000	30.1	42.8	48.4	72	88	107.2
20000	30.1	42.85	48.5	72	89	

Table IV.—Ionization of Potassium Iodide $\left(\alpha = \frac{\mu_v}{\mu_{max}}\right)$.

V.	0°.	18°.	25°.	50°.	65°.	78°.
10	0.49	0.47	0.458	0.41	0.38	....
12	0.51	0.485	0.475	0.42	0.40	0.37
16	0.54	0.51	0.497	0.45	0.42	....
32	0.615	0.58	0.567	0.52	0.48	....
64	0.69	0.65	0.641	0.60	0.56	....
128	0.765	0.73	0.722	0.69	0.64	(0.6)
250	0.80	0.795	0.788	0.765	0.71	....
500	0.88	0.86	0.855	0.84	0.78	....
1000	0.93	0.91	0.908	0.90	0.84	(0.85)
5000	0.997	0.99	0.986	0.99	0.98	....
10000	1.000	1.00	0.998	1.00	0.99	1.00
20000	1.000	1.00	1.000	1.00	1.00	1.00

The two extreme values at 78°, $V = 13.1$ and $V = 10000$, were the only results which I had time to determine by direct measurement in the sealed cells described above; the others are obtained by extrapolation and are naturally only rough approximations. Table IV. gives the degree of ionization calculated from the usual equation, $\alpha = \frac{\mu_v}{\mu_{max}}$. Compared with the values obtained by Prof. Jones,[1] by the boiling point method, the ionization found is decidedly higher, the dissociation of a decinormal solution being about 35 per cent against 25 per cent found by him, although the disagreement is much less than when the values for the conductivity are taken at lower temperatures. My own ebullioscopic determinations, as far as they have been carried, indicate approximately the same results as those of Prof. Jones.

The main interest in the above figures is in the values obtained at dilutions of over 10,000 liters. Up to 5,000 liters it is not only easy to obtain concordant results, but the values obtained, when plotted according to the Kohlrausch method against the reciprocal of the cube root of the volume, give, not a straight line as in the case of aqueous solutions of salts in the same interval of concentration, but a smooth curve slightly convex towards the dilution axis. Extrapolation from this would give a value of about $\mu_\infty = 56$ at 25° instead of 49, the highest reliable value obtained, and the values at 50,000 and 150,000 liters would be 52 and 53, respectively.

In the earlier series, before the source of error in the change of conductivity of the solvent due to the flasks cleaned in the old way was discovered, even higher (but discordant) values were obtained, from which it was thought that there might be a rapid increase in μ at very high dilutions, as has been surmised by other investigators using nonaqueous solvents. It is plain, however, that when the precautions described above are taken, the values, which agree as closely as could be expected where the correction for the conductivity of the solvent amounts to from 10 to 30 per cent of the whole, become practically constant between 20,000 and 40,000 liters and *decrease*

[1] Z. physik. Chem., **31**, 114 (1899).

at greater dilutions. This behavior is similar to that of acids and bases in aqueous solutions at about one-tenth the dilution, and may possibly be due, as is supposed in that case, to mutual interaction of the ions of solvent and solute.[1] Following the custom in the latter case, I have calculated the ionization from the *maximum* value of μ actually given by the experiments.

Thinking it possible that traces of water, such as must always be present even in the best alcohol, might produce a disproportionately great effect on the conductivity, 0.2 to 0.3 per cent by weight of conductivity water was added from a graduated 2 cc. pipette to some samples of alcohol, and to certain solutions. When due care was exercised to prevent contamination from the glass, the gain in conductivity did not exceed 0.01×10^{-6} and in some cases there was no change, or a slight decrease, from which it appears that minute traces of water cannot have any very deleterious effect. As a further test of this, three very dilute solutions were made up with the aqueous alcohol mentioned before, containing 0.8 per cent of water, and giving the very low conductivity 0.2×10^{-6}; at dilutions of 1760, 5500, and 22,000 liters the molecular conductivities 45.85, 47.5, and 44.2 were found, the first two being in close agreement with the values in absolute alcohol, the last agreeing with what would be found in the latter solvent at somewhat higher dilutions.

The results obtained with lithium chloride and bromide are given below; they are not believed to be as accurate as those with potassium iodide:[2]

Table V.—Molecular Conductivity of Lithium Chloride at 25°

Series I.		Series II.		Series III.		Series IV.	
V.	μ.	*V.*	μ.	*V.*	μ.	*V.*	μ.
36.1	20.6	11.37	15.1	67.3	22.5	33.9	19.8
192.0	28.5	85.5	24.2	336.5	29.6	637	31.2
6000	39.1	5345	35.9	5610	36.0	39800	37.1
24000	37.3			33650	39.1		

[1] Whetham: Z. physik. Chem., **88**, 200 (1906).

[2] The lithium chloride gave only 78.9 per cent chlorine instead of the calculated 83.4, from which it appears to have been somewhat basic. In the case of lithium bromide allowance had to be made for 24 per cent of water in salt.

Table VI.—Ratios of Molecular Conductivity of Lithium Chloride to μ_{25}.

V.	20°.	35°.	65°.
11.37	....	....	1.56
36.1	0.88	1.15	1.59
192.0	0.91	1.15	1.63
5345	....	....	1.88
6000	0.88	1.13	1.77

Table VII.—Molecular Conductivity and Ionization of Lithium Chloride.

V.	μ_{25}.	α_{25}.	μ_{65}.	α_{65}.
10	15	0.39	..	..
12	16.0	0.42	24	0.33
16	17.1	0.45	..	..
32	19.8	0.52	..	..
64	22.6	0.59	..	..
128	26	0.68	..	..
250	29	0.76	48	0.67
500	31.5	0.83	..	..
1000	33.5	0.88	..	..
5000	37	0.97	68	(0.95)
10000	37.5	0.99	..	..
20000	38	1.00	(72)	(1.00)

Table VIII.—Molecular Conductivity and Ionization of Lithium Bromide at 25° and 65°.

V.	μ_{25}.	μ_{65}.	$\mu_{65} \div \mu_{25}$.	α_{25}.	α_{65}.
14	18	30	1.66	0.44	0.4
54	25	43	1.70	0.61	0.57
5400	41	75	1.84	(1.00)	(1.00)

Summary of Results.

1. The precautions necessary to obtain reliable results for the conductivity of alcoholic solutions up to dilutions of 20,000 to 50,000 liters have been ascertained. A source of error in the contamination from glass vessels in which water has been dried has been pointed out.

2. The conductivity of potassium iodide has been measured up to 450,000 liters and the molecular conductivity has been shown to reach a maximum of 48.5 ± 0.5 reciprocal ohms at 25° at about 20,000 liters. A similar maximum appears to exist at all temperatures.

3. From measurements at 0°, 15°, 20°, 25°, 50°, 65°, and two measurements in sealed cells at 78°, the ionization coefficients have been calculated for all concentrations and temperatures up to the boiling point.

4. The temperature coefficients increase with rising temperature, slightly for the stronger solutions and much more noticeably for very dilute solutions. At any given temperature the temperature coefficient increases with increasing dilution.

5. The ionization decreases considerably with rising temperature. A 0.1 normal solution is dissociated 49 per cent at 0°, 46 per cent at 25°, and about 35 per cent at the boiling point.

6. The temperature coefficient for pure alcohol is much less than for alcohol with a conductivity of 0.3×10^{-6} reciprocal ohms: it may even be negative.

I desire to express here my thanks to Professor H. C. Jones for facilities granted to me and for his friendly interest in the above research.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
Nov. 3, 1908.

REVIEWS.

STEREOCHEMISTRY. By A. W. STEWART, D.Sc., Carnegie Research Fellow, and Lecturer on Stereochemistry in University College, London. Text-books of Physical Chemistry. Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S. London: Longmans, Green, and Co. 1907. pp. xx+583. Price, $2.80.

This is one of the latest volumes in the series of Text-Books of Physical Chemistry edited by Sir William Ramsay, and the student familiar with the excellent volumes by Findlay, Sydney Young, and others, will approach it with sanguine expectation. He will be disappointed. Instead of a readable and suggestive introduction to stereochemical science, a critical résumé of work done, and a stimulating formulation of problems not yet solved, he will find a collection of hurriedly written lecture notes, more or less disconnected, sometimes contradictory.

On p. 16 is given the principle, which is by no means true, that a compound cannot be active unless it contains an asymmetric carbon atom. Again, Chapter VI. (pp. 91–93) deals

with the inosites as an "exceptional" case of optical activity. Yet on p. 87 we find the necessary and sufficient condition of optical activity correctly stated in the words of Hartwall.

On pp. 21–22 one searches in vain for a critical estimate of the concept of pseudo-asymmetry. What object does it serve? What phenomena not otherwise intelligible does it correlate?

On p. 49 we read: "As a rule both optical antipodes have exactly the same chemical actions upon inactive bodies. A few statements to the contrary are to be found in the literature but it is *possible* that they may be due to errors of observation." Indeed, such observations cannot be anything else than erroneous, and the sooner the student realizes this the better.

No less than ten pages (pp. 66–76) are devoted to the configuration of the aldoses. Yet on p. 73 we read: "From the results of other investigations, which it is not necessary to discuss here, Fischer has deduced that a close relationship exists between the pentose configurations * * * * and the hexose formulae." In other words, after ten pages of hard labor the student's knowledge of Fischer's simple demonstration will still be incomplete.

The chapter on steric hindrance is comprehensive and the most likely to prove useful, although here, too, the author might be more scrutinizing in his treatment of the subject.

The rotatory power of substances is dealt with very briefly. On pp. 11–12, however, an attempt is made to give the student an elementary working knowledge of the nature of polarized light by likening it to a paper-cutter which will pass into a book if held parallel to the covers, but will refuse to pass into the book if held at its side perpendicularly to covers and leaves. The student who needs such illustrations at all will conclude that polarized light must refuse to pass through a tourmaline plate in all directions but one. If the book is addressed to beginners, a much longer (and better) explanation should have been given. If the reader is assumed to be mature, he will either need no explanation at all, or else know how to find one in a text-book of physics.

While Stewart's book, or at least this first edition of it, cannot be welcomed with enthusiasm, one must bear in mind that much in stereochemical science is in a nascent state, and that the task of writing a good treatise on the subject is a difficult one. The investigator ought to place the new book on his shelves beside Werner's well known *Lehrbuch*, on the principle that if one single suggestion can be gleaned from the pages of a book it is worth having.

M. A. ROSANOFF.

PHOTOCHEMIE UND BESCHREIBUNG DER PHOTOGRAPHISCHEN CHEMIKALIEN. Von H. W. VOGEL. Fünfte, völlig umgearbeitete Auflage, besorgt von DR. ERNST KÖNIG. Berlin: Gustav Schmidt. 1907. pp. XII + 376. Price, 11 M.

This volume forms Part I. of the "Handbuch der Photographie" and is devoted for the most part to the action of light upon the elements, organic and inorganic compounds, life processes of plants and animals, etc., regardless of their connection with photography. The first chapter treats of photo-crystallization, phosphorescence, Warnerhe's photometer, the action of light on selenium, Bell's photophone, Korn's system for telegraphing photographs, Sommerville's imagined production of magnetism by light, which is recorded as a fact, although it was repeatedly disproved twenty years ago, photo-electricity, Crooke's radiometer, and the action of X-rays and the radiations from radium.

The second chapter is devoted to the chemical action of light upon the elements and their compounds, and takes up decompositions, syntheses, and polymerizations which result from the action of light. Later on we find a very complete treatment of the behavior of the chemicals commonly used in photographic processes, and the behavior of the various light-sensitive compounds of the metals, including, of course, the action of dyes in rendering plates sensitive to definite regions of the spectrum.

The book forms a useful compendium, though a number of remarkable phenomena, such as the Clayden effect, receive no mention. R. W. W.

METHODS AND DEVICES FOR BACTERIAL TREATMENT OF SEWAGE. BY WILLIAM MAYO VENABLE. New York: John Wiley and Sons. 1908. pp. VI + 236. Price, $3.00.

This little volume by W. M. Venable, concerning the bacterial treatment of sewage, is an important addition to our list of text-books dealing with this subject and contains a full exposition of the essential principles underlying this process. The ideas are presented in a clear systematic manner, appealing especially to those with limited time at their disposal, and there is a happy combination of practical and scientific knowledge rarely seen in books of this character. The various means by which crude sewage may be purified are taken up in considerable detail, Chapter 3, for instance, considering the aerobic and Chapter 4 the anaerobic treatment of this material, other chapters dealing with such important subjects as the intermittent contact system, automatic discharging devices, and percolating filters. Two sections of the book are especially

to be commended—the one giving *seriatim* the various engineering principles involved in all systems of filtration, the other a detailed account of two actual installations, those at Fort DesMoines, Iowa, and Fort Leavenworth, Kansas, where the author was employed by the United States Government to oversee the construction of important sewage purification works. Mr. Venable's experience in these undertakings is extensively detailed, and in consequence this book becomes of great value to the practical engineer. W. W. FORD.

REFRIGERATION. By J. WEMYSS ANDERSON. New York: Longmans, Green, and Co. 1908. pp. 242. Price, $2.25.

In his introduction the author states that this work is intended to be an elementary treatise. With this in mind he has devoted the first six chapters to a general discussion of the effects produced by heat and to the thermodynamics of gases and of such vapors as are used in refrigeration. This is followed by a full description of the various types of refrigerating machines.

The subject of "Ice Making" and "Ice Making Plants" is treated at considerable length and many illustrations showing the interior of English ice plants are given. About twenty pages are devoted to the subject of cold storage and to the insulation of cold storage rooms.

Under "Marine Refrigeration" the most recent installations of refrigerating apparatus in such steamships as the Lusitania, Mauritania, Carmania, Tropic, and Cufic are described in detail and drawings of some of the outfits are given.

The book is written in such a way that it may be understood by one not technically educated. It contains much information that is valuable and will be found to be a good elementary text-book on Refrigeration. EDW. F. MILLER.

ELEVENTH ANNUAL CONVENTION OF THE ASSOCIATION OF STATE AND NATIONAL FOOD AND DAIRY DEPARTMENTS. Held at Jamestown Tercentennial Exposition, July 16–19, 1907. New York and London: John Wiley and Sons. 1908. pp. 416. Price, $3.00 net.

The reports of the meetings of this Association are always of interest as they bring together manufacturers of foods and officials charged with the inspection of foods. The questions are discussed both from the standpoint of the inspector and the manufacturer. A review of the proceedings is difficult because of the length of the program and the large number of questions treated. Among the interesting questions discussed may be mentioned: Publicity in the Enforcement of Pure-Food Laws, by Edward K. Slater, State Dairy and Food

Commissioner of Minnestoa; Coöperation between the State and Federal Authorities, by A. H. Jones, State Food Commissioner of Illinois; The Element of Uniformity in National and State Food Laws, by H. Q. Emery, State Dairy and Food Commissioner of Wisconsin; Diabetic Foods, by A. L. Winton, of the Chicago branch laboratory of the United States Department of Agriculture; "Like Substances," by James H. Shepard, State Analyst, South Dakota; Bleaching of Flour, by E. F. Ladd, State Commissioner of North Dakota.

Several addresses of special value to the dairy interests were given and difficulties experienced in the several States and by manufacturers in meeting the requirements of the laws of the various States were discussed. W. D. BIGELOW.